:00:09 OCA PAD AMENDMENT - PROJECT HEADER INFORMATION 04/04/95

Active

oject #: E-18-X13 Cost share #: Rev #: 2
nter # : 10/24-6-R8303-0A0 Center shr #: OCA file #: 251
Work type : RES
ntract#: DELIVERY ORDER 2 Mod #: LTR DTD 4/4/95 Document : DO
ime #: Contract entity: GTRC

bprojects ? : Y CFDA: NA
in project #: PE #: NA

oject unit: MSE Unit code: 02.010.112
oject director(s):
LOGAN K V MSE (404)894-3650

onsor/division names: ADVANCED ENGINEERED MAT INC / MARIETTA, GA
onsor/division codes: 250 / 057

ard period: 940915 to 950430 (performance) 950430 (reports)

onsor amount	New this change	Total to date
Contract value	0.00	29,258.00
Funded	0.00	29,258.00
st sharing amount		0.00

es subcontracting plan apply ?: N

itle: DEVELOPMENT OF TITANIUM DIBORIDE TECHNOLOGY - D.O. 2

PROJECT ADMINISTRATION DATA

A contact: Ina R. Lashley 894-4820

Sponsor technical contact

SAME
(000)000-0000

Sponsor issuing office

MR. JOHN R. WINTERS, PRESIDENT/CEO
(404)392-7849

ADVANCED ENGINEERED MATERIALS, INC
3419 CRANBORNE CHASE
MARIETTA, GA 30062-7413

ecurity class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): N
efense priority rating : NA NA supplemental sheet
quipment title vests with: Sponsor GIT X
NONE PROPOSED
dministrative comments -
SPONSOR LTR DTD 4/4/95 AUTHORIZES EXTENSION TO 4/30/95.

:00:10 SUBPROJECTS OF MAIN PROJECT E-18-X13 04/04/95

oject number	Spon/Div	Project Director	Total Contract	Project Unit	Total Funded
-9815	250/057	PATEL G R	22,802.00	EOEML	22,802.00

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 05/09/95

oject No. E-18-X13_____ Center No. 10/24-6-R8303-0A0_

oject Director LOGAN K V_____ School/Lab MSE_____

onsor ADVANCED ENGINEERED MAT INC/MARIETTA, GA_____

ntract/Grant No. DELIVERY ORDER 2_____ Contract Entity GTRC

ime Contract No. _____

tle DEVELOPMENT OF TITANIUM DIBORIDE TECHNOLOGY - D.O. 2_____

fective Completion Date 950430 (Performance) 950430 (Reports)

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loseout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	_____
Final Report of Inventions and/or Subcontracts	N	_____
Government Property Inventory & Related Certificate	N	_____
Classified Material Certificate	N	_____
Release and Assignment	N	_____
Other _____	N	_____

Comments_____
_____

ubproject Under Main Project No. _____

ontinues Project No. _____

istribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT (SUBPROJECTS)

Closeout Notice Date 05/09/95

ject No. E-18-X13 Center No. 10/24-6-R8303-0A0_

ject Director LOGAN K V_____ School/Lab MSE_____

nsor ADVANCED ENGINEERED MAT INC/MARIETTA, GA_____

---

ject # A-9815 PD PATEL G R Unit 01.021.740 T
DELIVERY ORDER 2 MOD# 4/4/95 E-MAIL EOEML *
21/24-6-R8303-000 Main proj # E-18-X13 OCA CO IRL
nsor-ADVANCED ENGINEERED /MARIETTA, GA 250/057
ELOPMENT OF TITAN
rt 940915 End 950430 Funded 22,802.00 Contract 22,802.00

END
* indicates the project is a subproject.
I indicates the project is active and being updated.
A indicates the project is currently active.
T indicates the project has been terminated.
R indicates a terminated project that is being modified.

DEVELOPMENT OF TITANIUM DIBORIDE TECHNOLOGY

FINAL SUMMARY TECHNICAL REPORT

Submitted By:

Kathryn V. Logan, Ph.D.
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0245

April 28, 1995

AEM Project A9815
10/24 - 10/28

A. There were a total of 9 batches (73-81) produced this week. The supplies from Dr. Logan's storage helped produce the batches. The data on masses and averages is contained in the attached data sheets.

B. On Wednesday Gautham and Charles and Dr. Logan traveled to Roswell and picked up the majority of the supplies in Dr. Logan's storage room. This included 9 cases of TiO2 and 7 cases of B2O3. The two reaction chambers were also picked up. There is an inventory list with Dr. Logan. The materials were unloaded at Baker and the rest was offloaded at 78H.

C. This week lab 108 in 78H has been almost completely cleaned by Charles and basically needs scrubbing before it can be occupied. Most of the surplus items have been organized in the lab and a good deal of Organic Chem. supplies were given to Mario Occelli in Baker. This included mainly funky looking glassware and molecular sieve. All of the burned out lights have been changed but two of the light fixtures are not working. The hoods have not been fixed yet either. The leak is still prevalent and may be coming from the water heater. Environmental Safety has been called concerning the Trancite and the Asbestos box. The four counter cabinets in the back corner have been moved outside on the side of the building. Henry Paris said to contact Surplus about taking them. He is worried about them getting rained on so they will probably be put somewhere inside the bay area until further notice.

D. The request for the roller enclosure has been placed by Charles at the Physical Plant.

E. A layout concerning space requirements has been made to help Henry Paris and AEM understand our needs in 78H.

F. Six cases of B2O3 has arrived but the TiO2 is still on back-order.

G. 600 pounds of Aluminum has arrived from Alcoa.

H. BET Surface Analyzer will require reprogramming according to Geoving. He will need 1/2 -1 day of personal time to rewrite the program. He may also need extra time for testing of the program.

I. There have been two batches ball milled for each time period of 8 hours, 15 hours and 30 hours. There should be plenty of material to hot press two disks for each time period.

AEM PROJECT A9815

BATCH	MASS	PERCENT	BALL MILL	PART	XRD	OBSERVATIONS
1	357.2	88.86			yes	This reaction was done before I started working.
2						Ditto.....
3						The materal seemed grainy and damp. The sample was not used
4			FAIL 30			This reaction, and each after, was ground in the mortar to insure uniform mixing because of the dampness of the TiO2. This sample was lost during ball milling.
5			FAIL 15			The B2O3 needs grinding because of clumping. It does not seem damp.
6			HR 8		yes	The solid was a bit more brittle.
7			HR 30		yes	Normal reaction.
8			HR 15		yes	The reaction was a little violent. This was assumed to come from an extended mixing time. The ash was whiter than usual.
9	366.2	91.09				Normal reaction (with grey ash).
10	364.2	90.60				Normal reaction.
11	367	91.29				The green flames lasted longer than normal. The solid had a strange design in the middle. This is assumed to be concen. B2O3 (see notebook).
12	366	91.04			yes	The reaction was very short and violent with a "whoosh". There were mushroom shaped lumps in the solid (see notebook).
13	378.1	94.05			yes	Normal reaction.
14	373.7	92.96				The TiO2 was lumpy and damp so the reaction was short and violent. The ash was brown.
15	378.4	94.13				Normal Reaction.
16	382.5	95.15				Normal Reaction.
17	378.1	94.05				Normal Reaction.
18	381.4	94.88				The reaction was short and calm with little smoke.
19	364.1	90.57				Normal reaction.
20	386.5	96.14				Normal reaction.
21	381	94.78				Normal reaction.
22	382.4	95.12				The flames had more orange. The ash was brown.
23	359.9	89.53				Normal reaction.

24	384	95.52		Normal reaction.
25	363.6	90.45		Normal reaction. The flames had more orange.
26	370	92.04		Normal reaction.
27	382.2	95.07		Normal reaction with the solid being a little more dense.
28	381.7	94.95	HR 8	Normal reaction.
29	381.7	94.95	HR 8	Normal reaction.
30	381.2	94.83	HR 8	Normal reaction.
31	389	96.77		Normal reaction.
32	374.9	93.26		Normal reaction.
33	385.4	95.87		Normal reaction.
34	390.4	97.11		I assumed that a white layer on the bottom of the solid was silica so I scraped it off.
35	362.1	90.07		Normal reaction.
36	375.2	93.33		A little more violent.
37	381.2	94.83		Normal reaction.
38	373.2	92.84		Normal reaction.
39	378.3	94.10		Normal reaction.
40	386.9	96.24	HR 15	Normal reaction.
41	387	96.27	HR 8	The flame was less green this time.
42	384.9	95.75	HR 30	Green spurts of flame lasted 15-30 seconds after the reaction (see p 60)
43	386.7	96.19		Small spurts of flame lasted for 1 1/2 min after the main reaction.
				Some small bursts rocked the crucible several times.
44	384.5	95.65		Normal with only two spurts after the reaction.
45	385.5	95.90		Short and normal.
46	386.9	96.24		Normal reaction.
47	386.4	96.12		Normal reaction.
48	392.3	97.59		Normal reaction.
49	384.9	95.75		Short with a whoosh.
50	388.8	96.72		Normal reaction.
51	385.5	95.90		Normal reaction. There was a blue solid built up on the wires after the reaction.
52	388	96.52		Very fast reaction.
53	390.5	97.14		Normal reaction.

***54	575.8	95.49	***	YES	Normal reaction.
55	386.4	96.12			Fast and furious reaction with 1 1/2' flames. Some lingering flames might have been a result of the powder on the side of the crucible.
56	395	98.26			Normal reaction.
57	388.2	96.57			Normal with smaller whiter flames.
58	0				This sample was discarded. The powder must have been misweighed because it was 50-60g underweight and was a sickly grey/purple color, It was very dense.
59	390.3	97.09			A little violent with two "pops" in the reaction.
60	388.9	96.74			Normal reaction.
61	386.9	96.24			Normal reaction.
62	385.3	95.85			Normal reaction.
63	385.1	95.80			Normal reaction.
64	386	96.02			Normal reaction.
65	390.8	97.21			Fairly violent with green flames.
66	384.7	95.70			Normal reaction.
67	391.3	97.34			Normal reaction.
68	389.7	96.94			The reaction started slowly and accelerated to green shooting flames with a "pop".
69	391.1	97.29			Very violent with a lot of smoke.
70	388.7	96.69			Normal reaction.
71	392.8	97.71			Normal reaction.
72	389.8	96.97			Normal reaction.
73	380.1	94.55			Very calm reaction. All of the powders are from K.L.'s storage and are oven dried in pans
74	390.1	97.04			Fast but normal reaction. The ash was very white.
75	391.2	97.31			Normal reaction. White ash.
76	388.5	96.64			Normal reaction. White ash.
77	385.1	95.80			Normal with calm tall flames. White ash.
78		0.00			Normal reaction.
79		0.00			Normal reaction.
80		0.00			Normal reaction.
81		0.00			Normal reaction.
82		0.00			Normal reaction.

AVG	AVG %
382.14	93.68

Weekly report Venkatesh Sundaram
(week of 10/24 - 10/31)

---

(1) AEM (Union Process) samples

The sample from AEM run #1(WC arms - 2 hours) was analyzed using SEM/EDS. The sample preparation method has been described in detail in an earlier report (dated 10/24). The objective was to determine the approximate amount of tungsten carbide (WC) contamination from the arms of the mill. The backscatter electron detector was inserted in the SEM. Since tungsten has a relatively higher atomic mass compared to either aluminum or titanium, the WC particles appear as very bright spots in the backscatter image. The minimum magnification at which the WC particles could be resolved was chosen and the number of particles observed in a finite number of random fields of view was recorded. The readings were noted at two different times and the observations are listed below. An accelerating voltage of 10 kV was used in both cases.

(1) Magnification - 5000 X.: # of fields of view = 25.
# of particles noticed = 8

area of one field of view = 20 ~~mm~~ μm X 30 ~~mm~~ μm 500 μm x 750 μm

(2) Magnification - 8000 X.: # of fields of view = 25
# of particles noticed = 6

= 10 μm x 15 μm 250 μm x 375 μm

The sample from AEM #4 (tool steel arms - 20 minutes) was also analyzed using EDS. The EDS results given in the previous report indicated contamination with silicon from the tool steel. Since there is not much difference in the atomic masses of Si, Al and Ti, there is not enough atomic number contrast in the backscatter image to resolve the silicon particles clearly. Hence, the above method used for sample #1 could not be used for this sample.

(2) Particle size analysis

The samples from milling (Union Process) using WC and tool steel arms had to be analyzed for particle size. The Microtrac laser analyzer in MSE was down and no work on particle size analysis could be done. The dispersing agent for sample preparation, Darvan #7, is available.

(3) X-ray diffraction of 600 gm batch sample

It was decided to repeat the XRD for the sample from the 600 gram batch to check for any additional peaks. One additional peak had been noticed in the first run last week. The reacted mass was ground in an alumina mortar and the powder was sieved through a 325 # to obtain very fine powder. This powder was then easily compacted to obtain the powder compact specimen for

the diffractometer. A step scan was used with a step size of 0.015^0 and a sample time of 1 sec to obtain a scan rate of about 1^0/minute. The results from the XRD are attached.

(4) A backscatter image of the sample AEM #1 (Union Process) is also attached. The bright particle at the center was analyzed using spot EDS and this confirmed the presence of tungsten.

DETECTED PEAKS FILE 31-OCT-94 10:03

APD with TAD

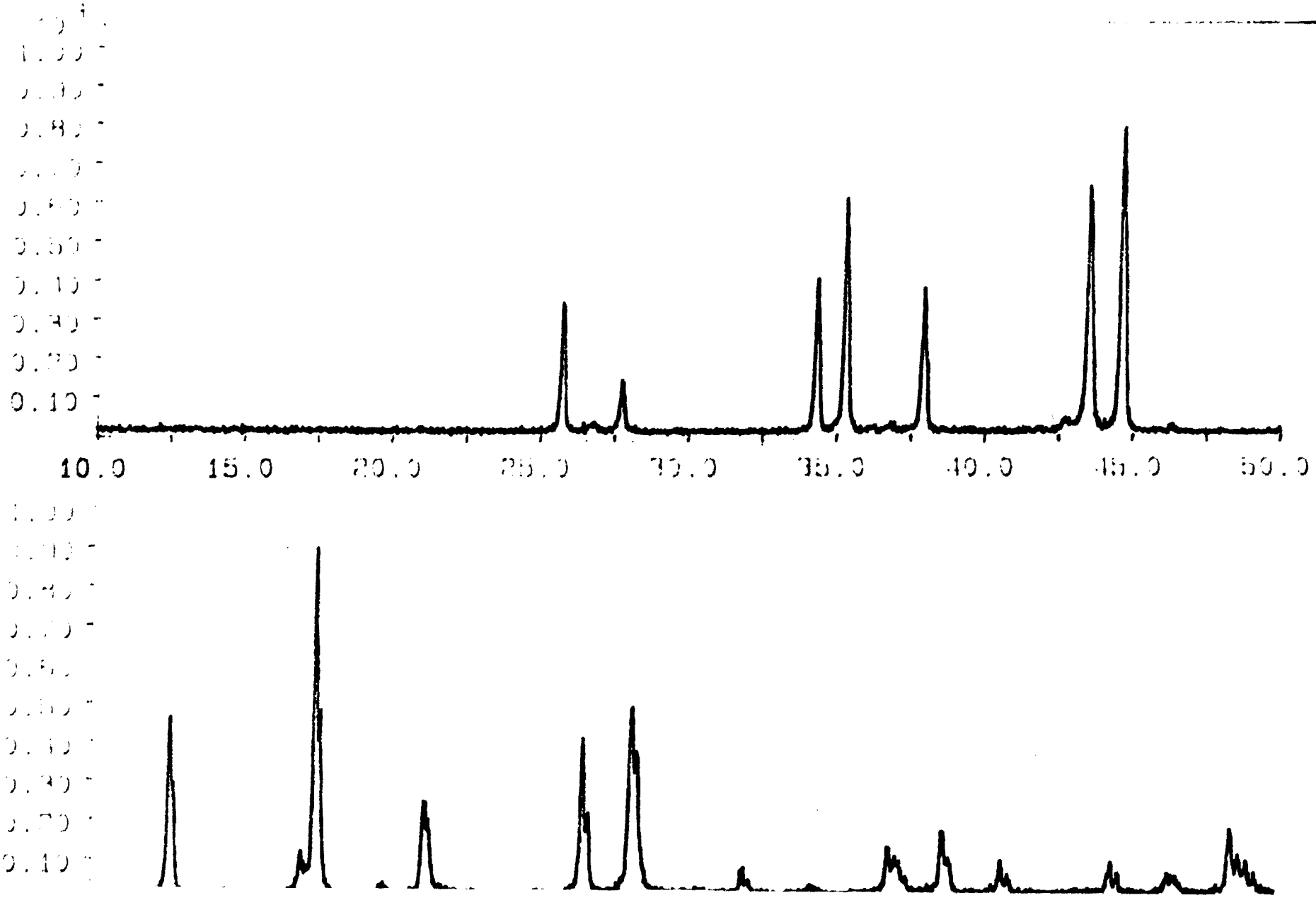
Listed DI file name : TA6002.DI
Original data file name : TA6002.RD
Sample identification : TA 600g #2
Measurement date/time : 31-OCT-94 7:39
Diffractometer system : 1
Generator settings : 40 kV, 30 mA
Cu alpha1,2 wavelengths : 1.54060, 1.54439 Ang
Step size, sample time : 0.015 deg, 1.00 s, 0.015 deg/s
Monochromator used : Yes
Divergence slit : Automatic (Irradiated sample length: 10.0 mm)

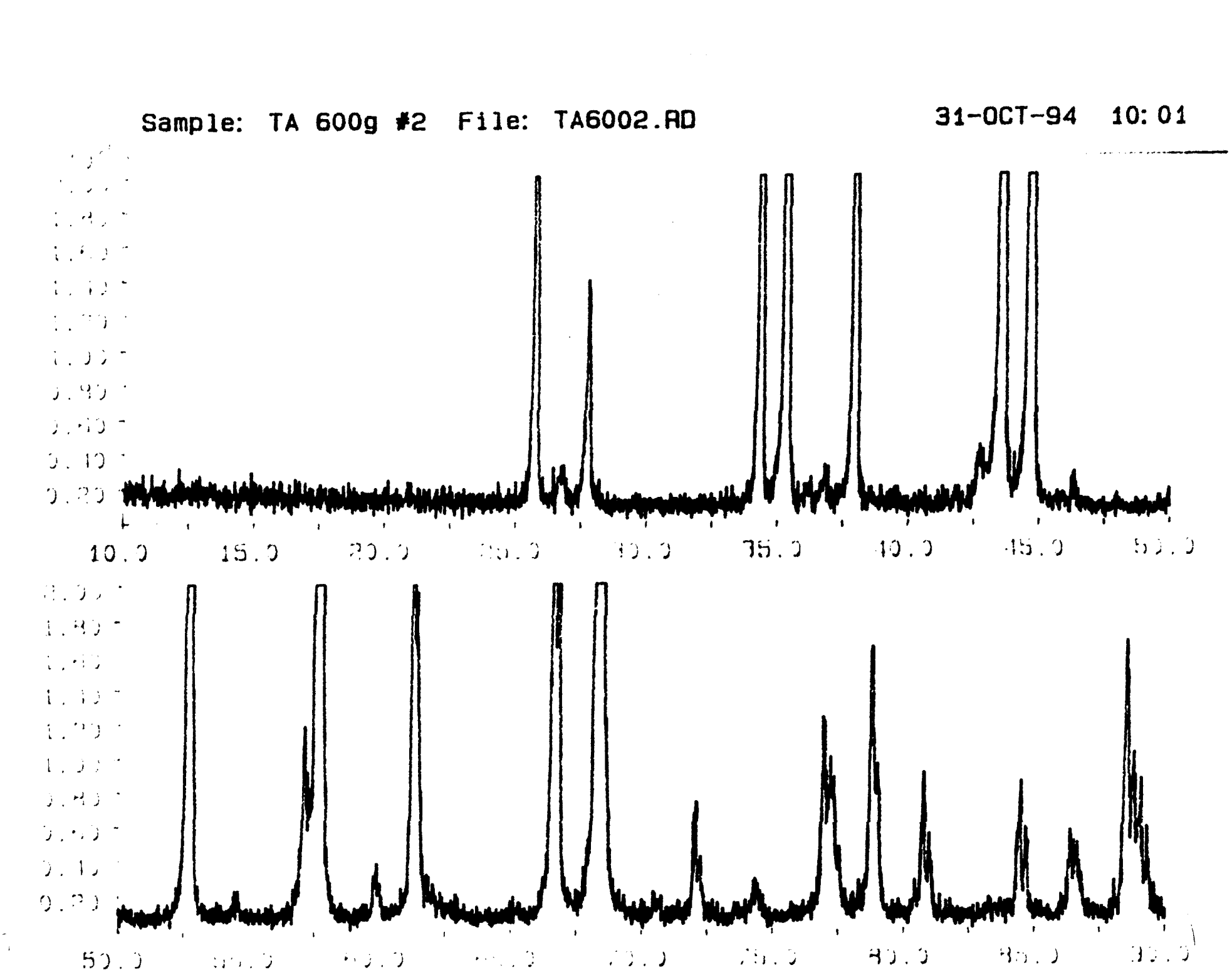
Analysis program number : 3
Peak angle range : 10.000 - 90.010 deg
Range in D spacing : 1.08927 - 8.8382 Ang
Peak position criterion : Top of smoothed data
Cryst peak width range : 0.00 - 2.00 deg
Minim peak significance : 1.00
Number of peaks in file : 47 (Alpha1: 31, Amorphous: 0)
Maximum intensity : 870. cts, 870.3 cps

Peak no	Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D spac (Ang)	I/Imax (%)	Type A1	Type A2	Type Ot	Sign
1	25.6925	0.07	292.	9.	3.4646	33.60	X			2.40
2	25.7650	0.07	262.	9.	3.4550	30.16	X	X		1.82
3	26.7600	0.18	19.	8.	3.3287	2.22	X	X		1.70
4	27.7375	0.10	117.	8.	3.2136	13.40	X	X		3.55
5	29.2150	0.10	10.	8.	3.0544	1.18	X	X		1.17
6	34.2925	0.12	369.	8.	2.6129	42.36	X	X		8.71
7	35.2600	0.12	552.	7.	2.5433	63.46	X			10.23
8	35.3575	0.07	335.	7.	2.5428	38.48		X		1.15
9	36.8125	0.24	17.	7.	2.4396	1.93	X	X		1.26
10	37.9100	0.07	350.	7.	2.3714	40.18	X			3.09
11	38.0275	0.04	146.	8.	2.3702	16.82		X		1.26
12	42.6950	0.18	30.	7.	2.1161	3.48	X	X		1.17
13	43.4575	0.10	581.	7.	2.0807	66.74	X	X		5.01
14	44.5775	0.15	745.	6.	2.0310	85.64	X			18.62
15	44.7325	0.07	335.	6.	2.0293	38.48		X		1.48
16	46.3350	0.18	12.	6.	1.9580	1.41	X	X		1.41
17	52.6450	0.10	449.	5.	1.7372	51.64	X			7.08
18	52.7950	0.09	253.	5.	1.7368	29.05		X		1.74
19	54.5200	0.30	11.	4.	1.6818	1.25	X	X		1.17
20	57.1075	0.09	104.	5.	1.6116	11.96			Ot	1.66
21	57.5925	0.10	870.	5.	1.5991	100.00	X			12.02
22	57.7600	0.06	437.	5.	1.5988	50.19		X		1.82
23	59.8225	0.15	27.	4.	1.5447	3.11	X	X		1.32
24	61.2250	0.07	213.	4.	1.5127	24.49	X			1.29
25	61.4325	0.09	164.	4.	1.5118	18.83		X		1.32
26	66.6250	0.10	396.	6.	1.4026	45.51	X			7.41
27	66.8250	0.10	199.	6.	1.4023	22.85		X		3.72
28	68.2350	0.07	424.	6.	1.3733	48.76	X			2.00
29	68.4950	0.04	313.	6.	1.3721	36.00		X		1.10

)	70.5975	0.36	10.	6.	1.3331	1.18	X	X	1.78
L	72.0250	0.09	58.	6.	1.3101	6.64	X		2.45
2	72.2475	0.18	28.	5.	1.3098	3.23		X	1.10
3	74.3400	0.21	18.	4.	1.2749	2.12	X	X	1.48
4	76.9400	0.10	112.	5.	1.2382	12.91	X		2.24
5	77.3050	0.24	74.	5.	1.2363	8.50		X	2.95
5	78.7600	0.16	156.	5.	1.2141	17.95	X		8.91
7	79.0275	0.12	76.	5.	1.2136	8.70		X	1.07
3	80.7375	0.06	79.	5.	1.1893	9.10	X		1.12
9	81.0075	0.12	37.	5.	1.1889	4.28		X	1.05
)	84.4750	0.06	76.	4.	1.1459	8.70	X		1.41
1	84.7325	0.09	48.	4.	1.1459	5.47		X	2.29
2	86.3875	0.09	42.	4.	1.1254	4.85	X		1.23
3	86.6875	0.24	34.	4.	1.1223	3.87	X	X	1.10
4	88.5050	0.06	159.	4.	1.1039	18.24	X		1.15
5	88.7950	0.09	86.	4.	1.1037	9.94		X	1.38
6	89.0675	0.06	79.	4.	1.0983	9.10	X		1.20
7	89.3675	0.09	36.	4.	1.0981	4.14		X	1.17

Sample: TA 600g #2 File: TA6002.RD 31-OCT-94 09:58




Sample: TA 600g #2 File: TA6002.RD
31-OCT-94 10:01
10.0
15.0
35.0
40.0
45.0
50.0

Dr. Logan,

I checked the extra peak in 500 g sample with some possible compounds.

I eliminated the following possibilities.

① Al (4-787) ← JCPDS #.

② B_2O_3 (# 6-634)

③ TiO_2 (Anatase) → (# 21-1272)

④ $TiBO_3$ → (13-710)

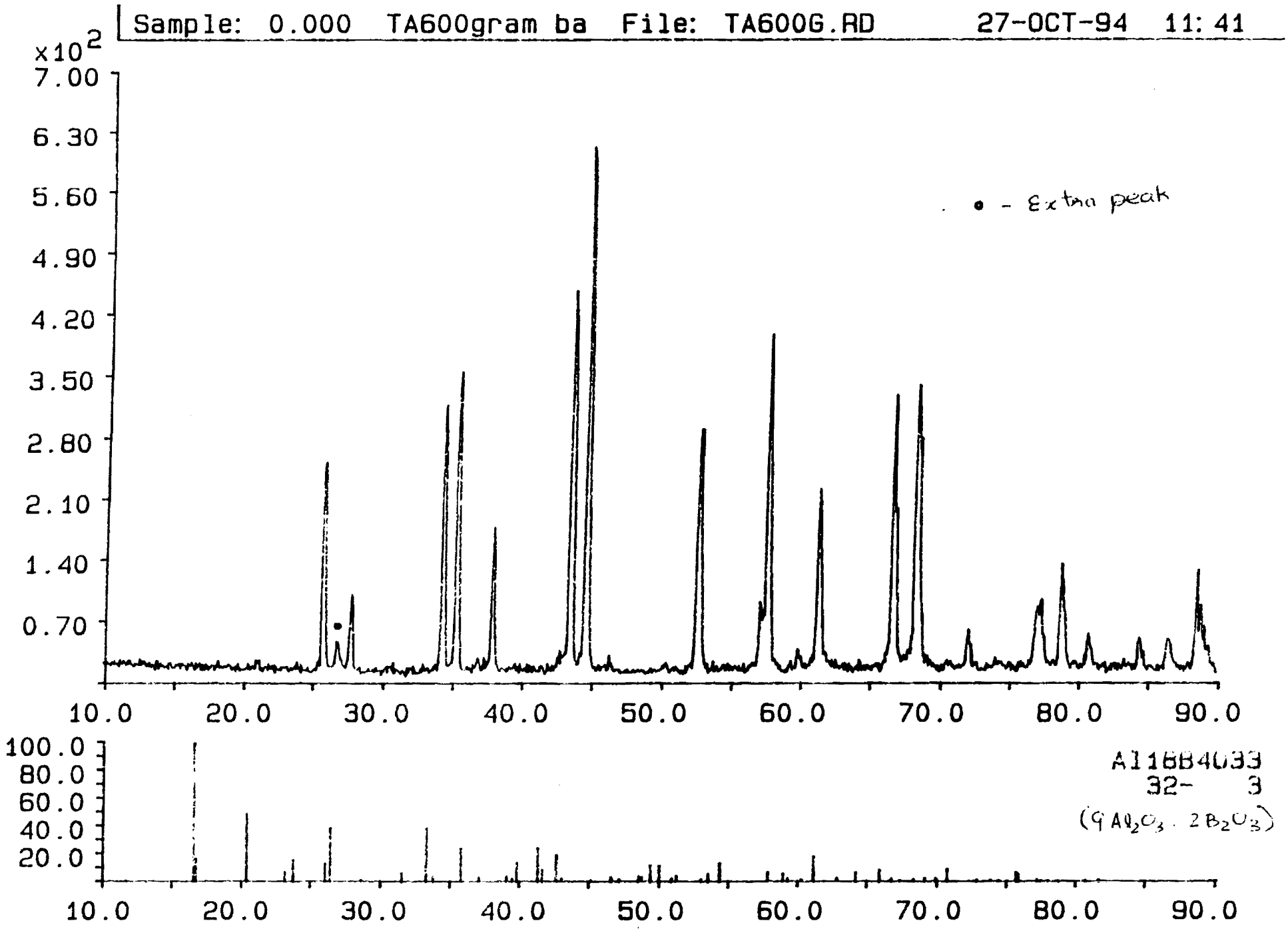
I've attached comparison plots for

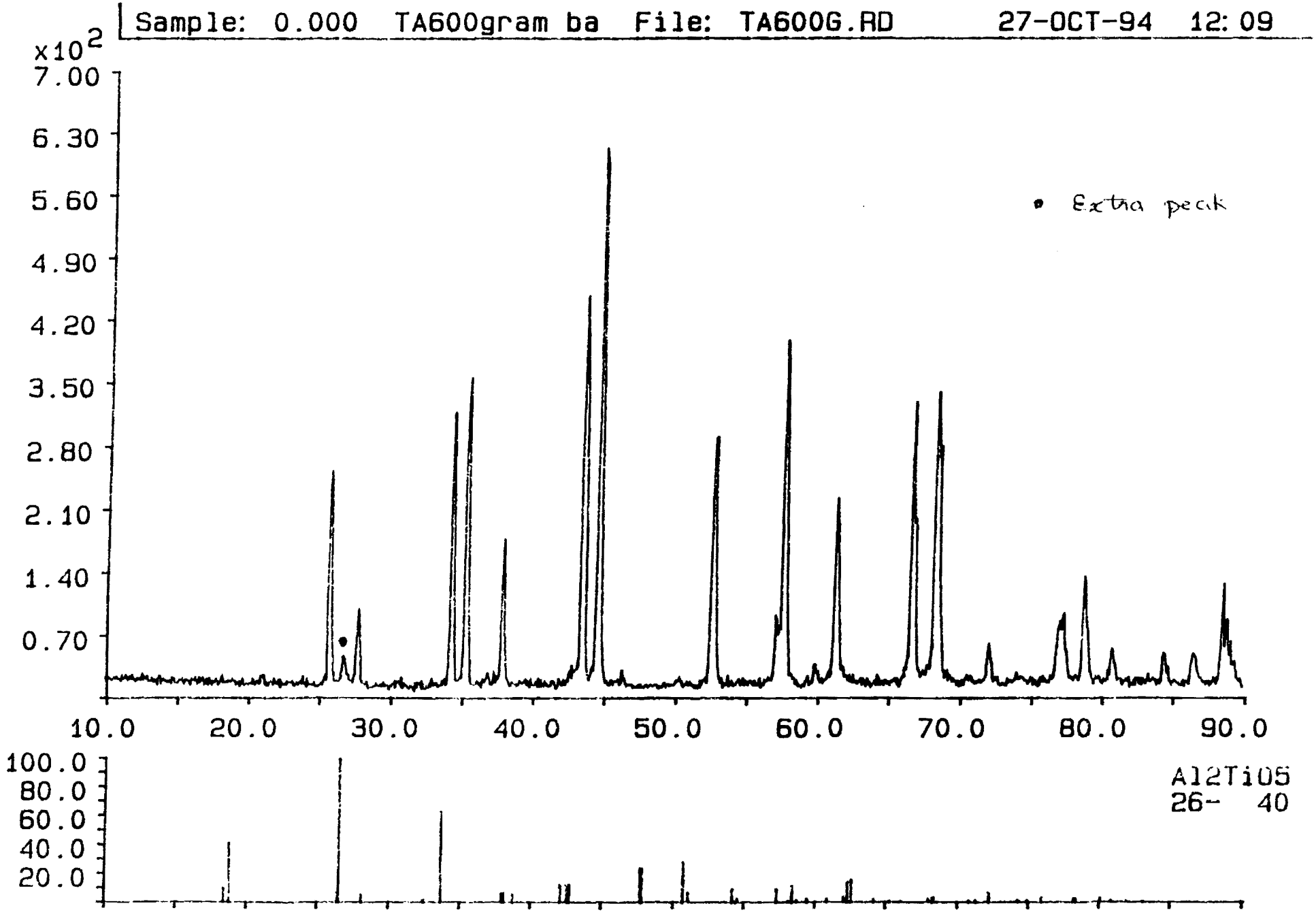
① $9Al_2O_3 \cdot 2B_2O_3$ (# 32-3)

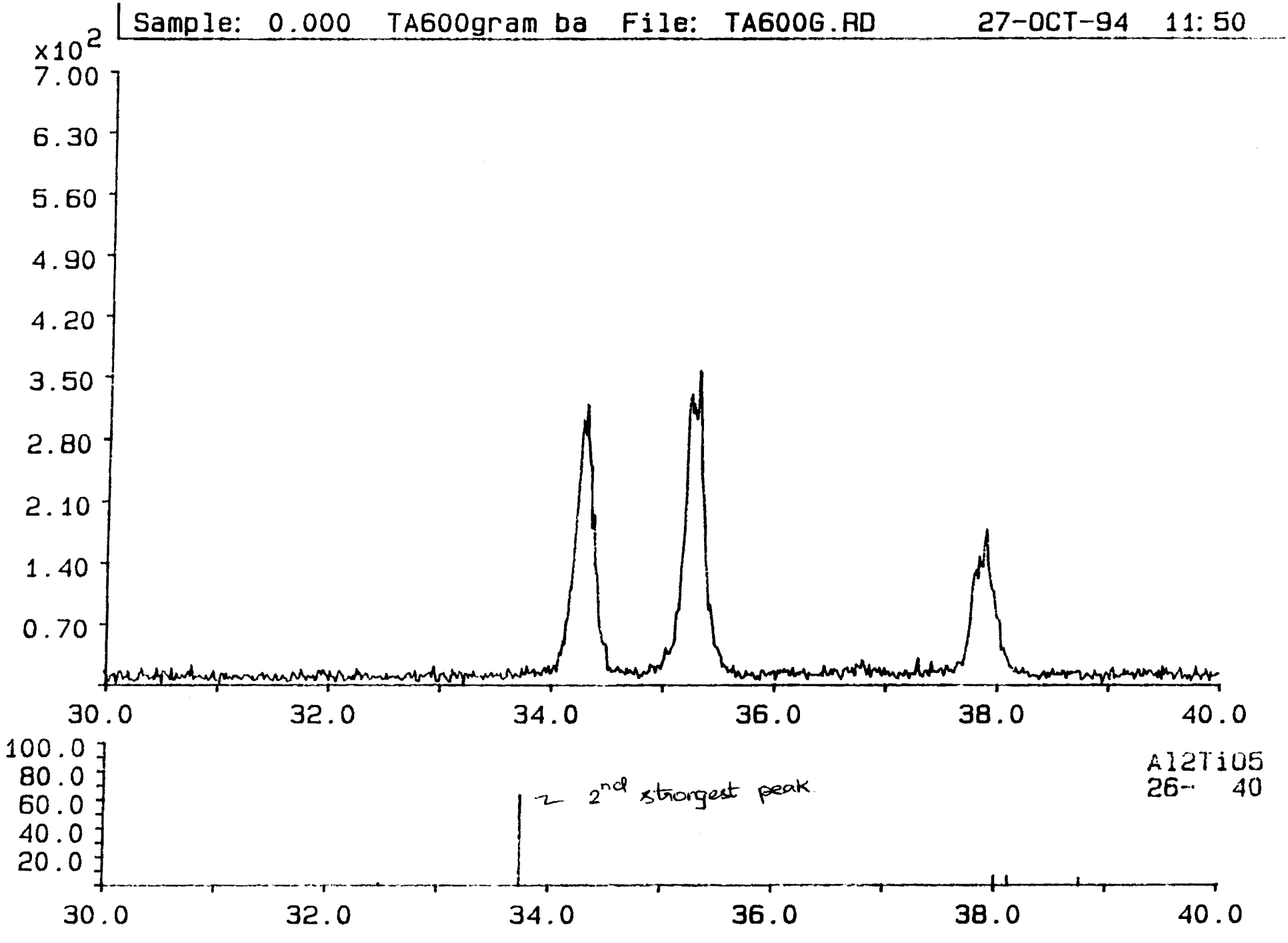
② Al_2TiO_5 (# 26-40)

Since the 100% peak in Al_2TiO_5 matches with the extra peak, I've made a comparison plot of the range of the second strongest Al_2TiO_5 peak. Does not seem to be anything there.

Venky


Sample: 0.000 TA600gram ba File: TA600G.RD 27-OCT-94 11:41
x10 2
7.00
6.30
5.60
4.90
4.20
3.50
2.80
2.10
1.40
0.70
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
• - Extra peak
100.0
80.0
60.0
40.0
20.0
A11BB4033
32- 3
(9 Al2O3 . 2 B2O3)


Sample: 0.000 TA600gram ba File: TA600G.RD 27-OCT-94 12:09
x10 2
7.00
6.30
5.60
4.90
4.20
3.50
2.80
2.10
1.40
0.70
Extra peak
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
80.0
60.0
40.0
20.0
Al2Ti05
26- 40


Sample: 0.000 TA600gram ba File: TA600G.RD 27-OCT-94 11:50
x10 2
7.00
6.30
5.60
4.90
4.20
3.50
2.80
2.10
1.40
0.70
30.0
32.0
34.0
36.0
38.0
40.0
100.0
80.0
60.0
40.0
20.0
2nd strongest peak
A12T105
26- 40

DETECTED PEAKS FILE 24-OCT-94 3:36

.pd test

Listed DI file name : TA600G.DI
Original data file name : TA600G.RD
Sample identification : 0.000 TA600gram ba
Measurement date/time : 17-OCT-94 18:33
Diffractometer system : 1
Generator settings : 40 kV, 30 mA
Cu alpha1,2 wavelengths : 1.54060, 1.54439 Ang
Step size, sample time : 0.015 deg, 1.00 s, 0.015 deg/s
Monochromator used : Yes
Divergence slit : Fixed (? deg)

Analysis program number : 3
Peak angle range : 10.000 - 90.010 deg
Range in D spacing : 1.08927 - 8.8382 Ang
Peak position criterion : Top of smoothed data
Cryst peak width range : 0.00 - 2.00 deg
Minim peak significance : 1.00
Number of peaks in file : 36 (Alpha1: 28, Amorphous: 0)
Maximum intensity : 566. cts, 566.4 cps

Peak No	Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D spac (Ang)	I/Imax (%)	Type A1	Type A2	Type Ot	Sign
1	20.8550	0.72	10.	10.	4.2560	1.81	X	X		1.15
2	25.6925	0.07	240.	10.	3.4646	42.41	X	X		2.45
→ 3	→26.7325	→0.24	→28.	→9.	→3.3321	→4.96	→X	X	→	→2.51→ ε
4	27.7425	0.18	77.	9.	3.2131	13.67	X	X		4.90 ρ
5	34.2825	0.12	299.	8.	2.6136	52.84	X	X		6.76
6	35.2250	0.04	317.	9.	2.5458	55.94	X			2.45
7	35.3150	0.04	289.	9.	2.5395	51.02	X	X		1.62
8	37.7925	0.06	114.	11.	2.3785	20.21	X	X		1.10
9	43.4125	0.07	412.	11.	2.0827	72.75	X	X		2.75
10	44.5475	0.13	566.	10.	2.0323	100.00	X			10.23
11	44.7025	0.06	317.	10.	2.0306	55.94		X		1.07
12	46.1225	0.72	10.	9.	1.9665	1.81	X	X		1.62
13	50.1425	0.72	10.	7.	1.8178	1.81	X	X		1.66
14	52.5450	0.04	216.	8.	1.7402	38.15	X			2.00
15	52.7375	0.04	279.	8.	1.7386	49.24		X		1.51
16	57.0600	0.15	64.	10.	1.6128	11.30	X	X		1.55
17	57.5025	0.06	317.	10.	1.6014	55.94	X			1.48
18	59.3525	0.24	18.	10.	1.5440	3.11	X	X		1.32
19	61.2300	0.09	185.	11.	1.5126	32.65	X			2.95
20	61.3350	0.09	161.	11.	1.5128	28.47		X		1.32
21	66.5925	0.07	306.	12.	1.4032	54.07	X			1.62
22	66.8150	0.06	159.	12.	1.4025	28.03		X		1.12
23	68.2675	0.04	310.	12.	1.3728	54.69	X			1.10
24	68.4600	0.09	216.	12.	1.3728	38.15		X		1.66
25	72.0875	0.36	37.	11.	1.3091	6.57	X	X		4.79
26	74.4400	0.72	10.	12.	1.2735	1.81	X	X		2.51
27	76.8400	0.12	66.	9.	1.2382	11.58	X			1.05
28	77.2900	0.12	77.	9.	1.2365	13.67		X		1.15
29	78.7625	0.12	106.	10.	1.2141	18.73	X			1.66

79.0450	0.09	55.	10.	1.2134	9.67		X	1.12
80.6875	0.15	37.	10.	1.1899	6.57	X	X	1.51
84.3800	0.18	35.	11.	1.1470	6.15	X	X	2.04
86.4675	0.42	35.	10.	1.1246	6.15	X	X	3.98
88.4975	0.18	100.	11.	1.1039	17.65	X		3.72
88.7800	0.12	67.	11.	1.1012	11.87	X	X	1.10
89.0525	0.12	49.	11.	1.1012	8.65		X	1.26

AEM Project A9815
10/31-11/4

A. All of the Composite reactions have been completed with a total of 82 reactions. This is a total of 69.1 pounds of Composite material. There has been enough material ball milled at 8, 15 and 30 hours to hot press two disks each. -22.3# to HP ≈ 46#

B. There have been 7 Pure TiB2 reactions as of Friday at noon. This gives us a total of approximately 10 pounds of Pure TiB2. As a whole they have been very violent with a good deal of ash produced. The solid is very porous and makes it difficult to remove the wire tainted solid. The average return seems to be about 510g for each 600g reaction, this is a return of about 85%. Alison has learned the reaction procedure and she and Venky have been doing production.

C. Guillermo has explained the hot pressing procedure to Charles but it needs to be done one more time so the procedure can be entered into the lab book. While we are waiting for the thermo couples to arrive we have been making graphite dies for the hot pressing. The milling machine works well but the metal lathe is very inaccurate. There has been one 3" die plunger milled for the 3" die mold that has been milled. All of the materials needed for hot pressing have been ordered.

D. The work order for the leak in 78H has been placed and a plumber was to check it out on Thursday. He will call the roofers if needed.

E. The Fisher masks will be used as soon as the filter retainers are received. They are due in to Fisher on the 16th. The other filter cartridges have been returned.

F. Samples of the first Pure reaction have been prepared for XRD. Venky will have the results from the 600g Composite sample and the results from the first Pure reaction.

G. The replacement parts for the Vacuum furnace have arrived. Geoving will replace the solenoids and Charles will replace the door seal with the help of Guillermo.

AEM PROJECT A9815

BATCH	MASS	PERCENT	BALL MILL	PART	XRD	OBSERVATIONS

AEM PROJECT A9815

BATCH	MASS	PERCENT	BALL MILL	PART	XRD	OBSERVATIONS
1	357.2	88.86			yes	This reaction was done before I started working.
2						Ditto.....
3						The materal seemed grainy and damp. The sample was not used
4			FAIL 30			This reaction, and each after, was ground in the mortar to insure uniform mixing because of the dampness of the TiO2. This sample was lost during ball milling.
5			FAIL 15			The B2O3 needs grinding because of clumping. It does not seem damp.
6			HR 8		yes	The solid was a bit more brittle.
7			HR 30		yes	Normal reaction.
8			HR 15		yes	The reaction was a little violent. This was assumed to come from an extended mixing time. The ash was whiter than usual.
9	366.2	91.09				Normal reaction (with grey ash).
10	364.2	90.60				Normal reaction.
11	367	91.29				The green flames lasted longer than normal. The solid had a strange design in the middle. This is assumed to be concen. B2O3 (see notebook).
12	366	91.04			yes	The reaction was very short and violent with a "whoosh". There were mushroom shaped lumps in the solid (see notebook).
13	378.1	94.05			yes	Normal reaction.
14	373.7	92.96				The TiO2 was lumpy and damp so the reaction was short and violent. The ash was brown.
15	378.4	94.13				Normal Reaction.
16	382.5	95.15				Normal Reaction.
17	378.1	94.05				Normal Reaction.
18	381.4	94.88				The reaction was short and calm with little smoke.
19	364.1	90.57				Normal reaction.

AEM PROJECT A9815

BATCH	MASS	PERCENT	BALL MILL	PART	XRD	OBSERVATIONS
20	386.5	96.14				Normal reaction.
21	381	94.78				Normal reaction.
22	382.4	95.12				The flames had more orange. The ash was brown.
23	359.9	89.53				Normal reaction.
24	384	95.52				Normal reaction.
25	363.6	90.45				Normal reaction. The flames had more orange.
26	370	92.04				Normal reaction.
27	382.2	95.07				Normal reaction with the solid being a little more dense.
28	381.7	94.95	HR 8			Normal reaction.
29	381.7	94.95	HR 8			Normal reaction.
30	381.2	94.83	HR 8			Normal reaction.
31	389	96.77				Normal reaction.
32	374.9	93.26				Normal reaction.
33	385.4	95.87				Normal reaction.
34	390.4	97.11				I assumed that a white layer on the bottom of the solid was silica so I scraped it off.
35	362.1	90.07				Normal reaction.
36	375.2	93.33				A little more violent.
37	381.2	94.83				Normal reaction.
38	373.2	92.84				Normal reaction.
39	378.3	94.10				Normal reaction.
40	386.9	96.24	HR 15			Normal reaction.
41	387	96.27	HR 8			The flame was less green this time.
42	384.9	95.75	HR 30			Green spurts of flame lasted 15-30 seconds after the reaction (see p 60)
43	386.7	96.19				Small spurts of flame lasted for 1 1/2 min after the main reaction.
						Some small bursts rocked the crucible several times.
44	384.5	95.65				Normal with only two spurts after the reaction.
45	385.5	95.90				Short and normal.

AEM PROJECT A9815

BATCH	MASS	PERCENT	BALL MILL	PART	XRD	OBSERVATIONS
46	386.9	96.24				Normal reaction.
47	386.4	96.12				Normal reaction.
48	392.3	97.59				Normal reaction.
49	384.9	95.75				Short with a whoosh.
50	388.8	96.72				Normal reaction.
51	385.5	95.90				Normal reaction. There was a blue solid built up on the wires after the reaction.
52	388	96.52				Very fast reaction.
53	390.5	97.14				Normal reaction.
***54	575.8	95.49	***		YES	Normal reaction.
55	386.4	96.12				Fast and furious reaction with 1 1/2' flames. Some lingering flames might have been a result of the powder on the side of the crucible.
56	395	98.26				Normal reaction.
57	388.2	96.57				Normal with smaller whiter flames.
58	0					This sample was discarded. The powder must have been misweighed because it was 50-60g underweight and was a sickly grey/purple color, It was very dense.
59	390.3	97.09				A little violent with two "pops" in the reaction.
60	388.9	96.74				Normal reaction.
61	386.9	96.24				Normal reaction.
62	385.3	95.85				Normal reaction.
63	385.1	95.80				Normal reaction.
64	386	96.02				Normal reaction.
65	390.8	97.21				Fairly violent with green flames.
66	384.7	95.70				Normal reaction.
67	391.3	97.34				Normal reaction.
68	389.7	96.94				The reaction started slowly and accelerated to green shooting flames with a "pop".
69	391.1	97.29				Very violent with a lot of smoke.
70	388.7	96.69				Normal reaction.

AEM PROJECT A9815

BATCH	MASS	PERCENT	BALL MILL	PART	XRD	OBSERVATIONS
71	392.8	97.71				Normal reaction.
72	389.8	96.97				Normal reaction.
73	380.1	94.55				Very calm reaction. All of the powders are from K.L.'s storage and are oven dried in pans
74	390.1	97.04				Fast but normal reaction. The ash was very white.
75	391.2	97.31				Normal reaction. White ash.
76	388.5	96.64				Normal reaction. White ash.
77	385.1	95.80				Normal with calm tall flames. White ash.
78	390.8	97.21				Normal reaction.
79	388.3	96.59				Normal reaction.
80	390.3	97.09				Normal reaction. Grey ash.
81	385.7	95.95				Normal reaction. White ash.
82	578.2	96.59				Very violent and green.

AVG	AVG %
382.51	95.15

PURE POWDER

83	501.4	83.57	Very violent reaction with two "pops". A lot of grey ash.
84	501.2	83.53	Very violent withe three "pops". A lot of brown ash.
85	517.2	86.20	Fairly calm with a good deal of brown ash produced.
86	511.6	85.27	Medium calm with one "pop". Still a lot of ash.
87	516	86.00	

AVG	AVG%

AEM PROJECT A9815

BATCH	MASS	PERCENT	BALL MILL	PART	XRD	OBSERVATIONS
	509.48	84.91333				

AEM PROJECT 19815
11/14-11/18

A. There have been 27 batches of TiB2 made to date. These have averaged 511.81 g gross and 494.89 net per batch. The results ar skewed somewhat after the 3-4 bad reactions. The reactions are very calm with very little smoke and flame now. There is 27.25 lbs of powder made not including the three reactions still unweighe d.

B. There has been two 8 hour composite ball mill runs as of Friday for a total of about 5-6 lbs of powder. More rubber gasket seal is needed for ball mill C. All of he mills have approximately the same amount of balls in them.

C. There have been two hot press runs done this week for a total of three disks made. The second run ended with an automatic shutdown when the water exchanger failed to cool the coil sufficiently. The third run ran a complete cycle and ended with a % dense of 93.7%. The settings for the press can be found on the hot press data sheet.

D. The leaching is ready to start except the fume hoods have not been repaired yet. The work order was placed several weeks ago but nothing has been done. The matter was placed in the hands of Delora Gould and is expected to be finished by this week.

E. There have been two vacuum furnace runs for a total of 12 new crucibles. They are now in service. There has been two stainless steel pans received from Paul Sykes. Two cans of B2O3 have been received from BORAX. The powder is granular and coarse, unlike the powder received from Fisher.

PURE POWDER INVENTORY

TOTAL	MAS G		MASS LB	
	GROSS	NET	GROSS	NET
	10236	12372	22.55	27.25

	AVG G		AVG LB	
	GROSS	NET	GROSS	NET
	511.81	494.89	1.13	1.09

AVG %		
GROSS	NET	
77.55	76.37	NOTE: THESE ARE THE SAME BECAUSE THEY COME FROM DIFFERENT AMOUNTS OF RE

BATC	GROS NET		GROSS NET %		BALLMILL PAR	XRD

BATC PURE	GROS NET MASS		GROSS NET %		BALLMILL PAR	XRD
83		501.4		83.57		
84		501.2		83.53		
85		517.2		86.20		
86		511.6		85.27		
87		516		86.00		
88	535.9	525	89.32	87.50		
89	528.7	510.4	88.12	85.07		
90	525.8	449.3	87.63	74.88		
91	530	506.3	88.33	84.38		
92	391.4	368	65.23	61.33		
93	336	317	56.00	52.83		

AVG GROS MASS	AVG NET MASS	AVG %	AVG %
474.6	474.9	79.11	79.14

total g	total lbs
5223.4	11.51

KVL

AEM Project #A9815 (Pure TiB_2)
Weekly report
(week of 11/14 - 11/21)

Alison Carney
Venkatesh Sundaram

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(1) During the last week, a total of 13 pure TiB_2 reactions were performed yielding 15 pounds of powder. So far, a total of 27 reactions have been completed yielding a total amount of 28.5 lbs. of powder mixture ($MgO+TiB_2$). A detailed table of all the reactions is attached. It was observed that the reactions done on the 10th and 11th November (#10 to #14) were extremely violent and this resulted in a large reduction in the powder yield. The reason for this behavior is believed to be moisture in the magnesium powder, which was constantly exposed to humid air during weighing. A new batch of 50 lbs. of Mg powder has been obtained and this powder has been sealed in 10 paint cans. The powder from a paint can is transferred to bottles and used and this has resulted in reactions which are very calm and less violent than even the initial reactions (#1 to #9). Also, new batches of B_2O_3 and TiO_2 powders are being used. Some of the new bottles of B_2O_3 were lumpy when opened.

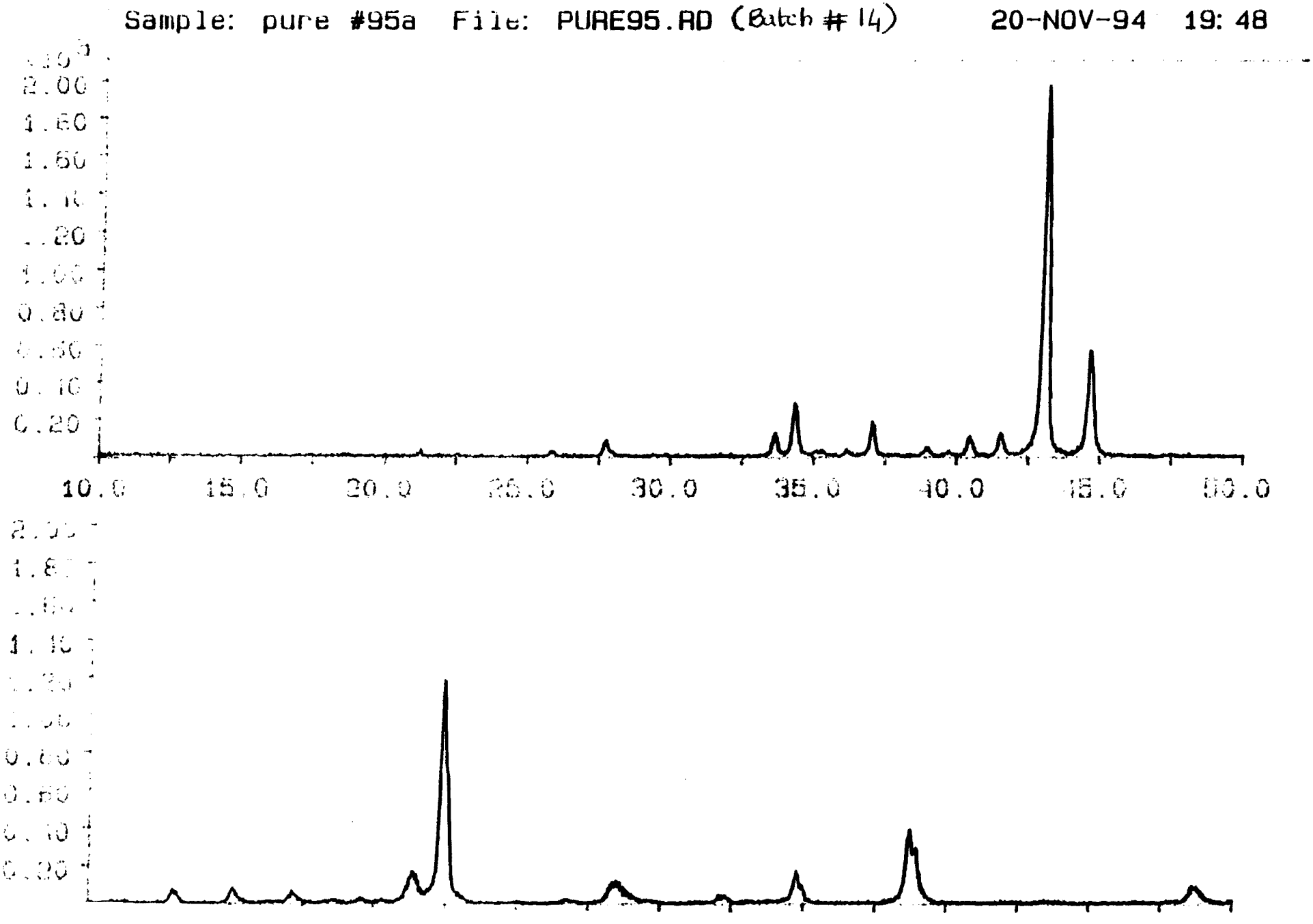
(2) A new set of crucibles was used last week. There are now a total of 7 sets of crucible tops and bottoms. This will ensure continuous synthesis of the powders. Also, about two cartons full of empty bottles were obtained from 78H and cleaned and dried. Some of the recent reactions resulted in high yields of more than 530 grams and so these batches had to be stored in two bottles each. It has been observed that the yield increases considerably on using dry starting powders and this also makes the mixing process easier. The powder mixing and sifting in the case of the pure reactions take considerably longer time and so only about four reactions can be done in a day.

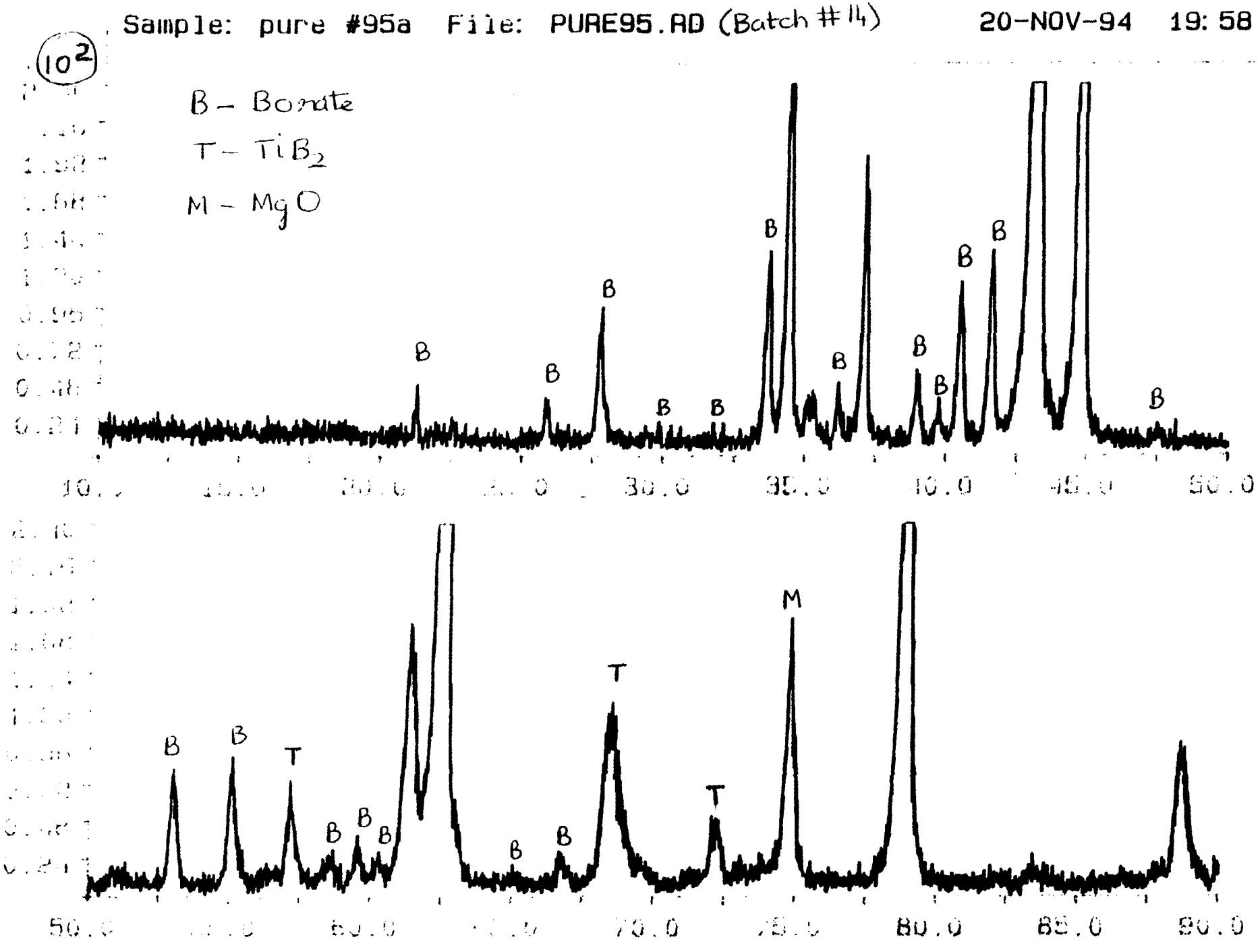
(3) X-ray diffraction results

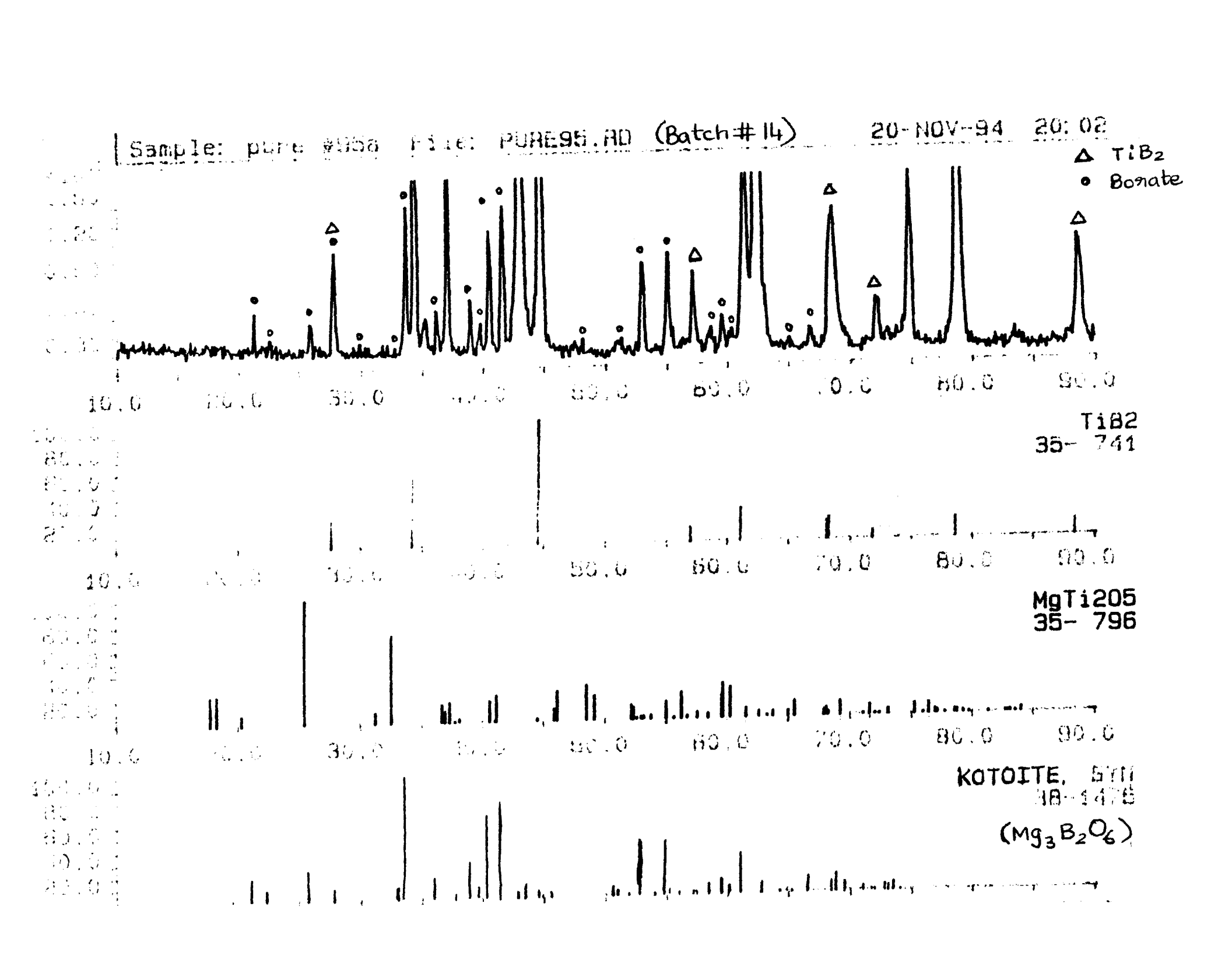
Samples were taken from batch #14 (violent reaction with low yield) and from batch #15 (first normal reaction with new powders) to check the products of the reaction. The sample preparation has been described earlier. The scan rate used was about 1^0/minute. The results from the XRD are attached. It is observed that the two patterns obtained are similar and are also consistent with patterns of earlier batches. The product from the violent reactions is similar to that from other reactions and can be used. The violence of the reaction seems to have affected only the yield. The product phases include TiB_2 and MgO with minor amounts of borate ($Mg_3B_2O_6$). Magnesium titanate has not been detected in the product.

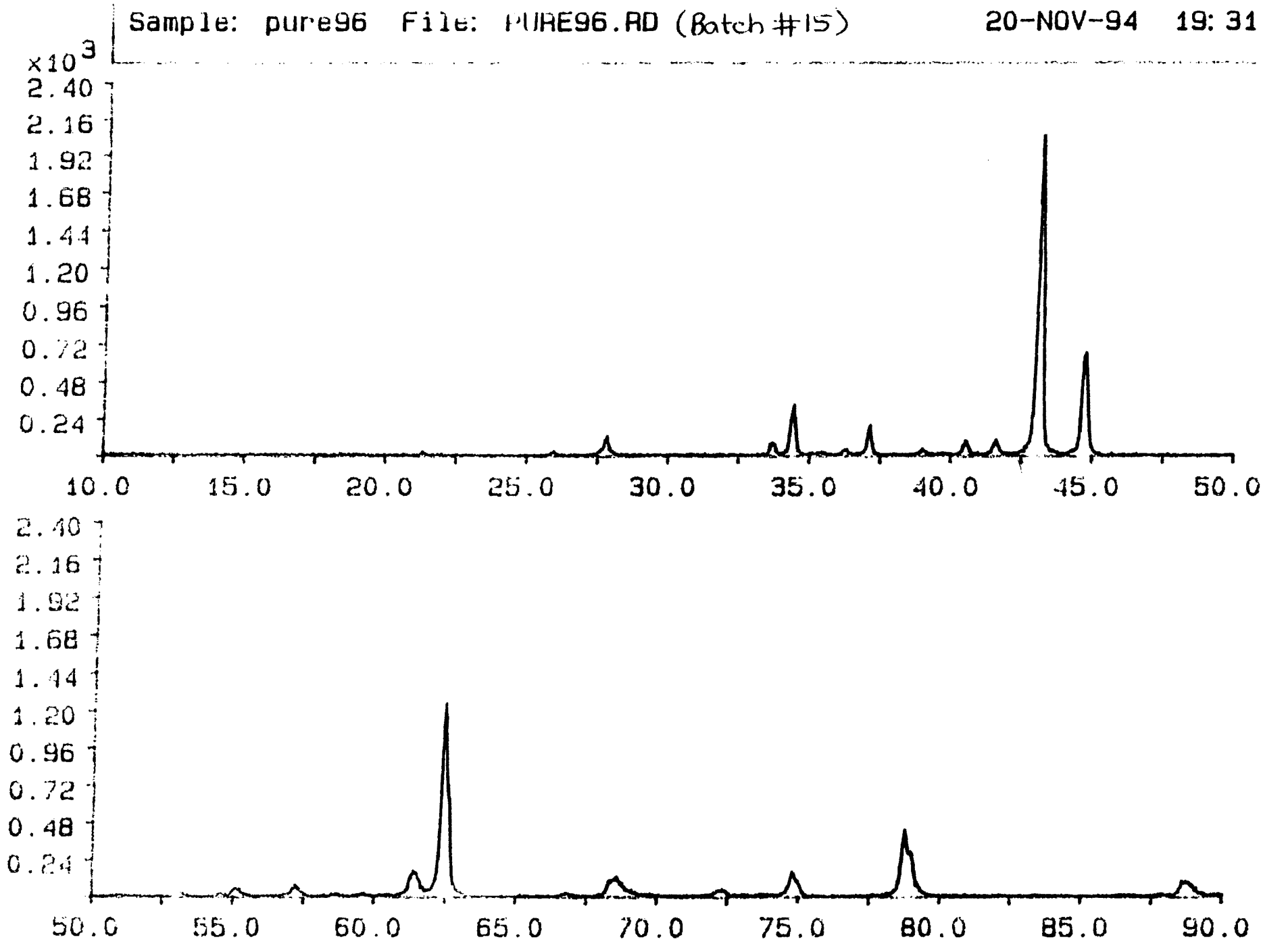
Batch #	Mass obtained (grams) (after reaction)	Yield (%) (after reaction)	Mass obtained (grams) (after bottling)	Yield (%) (based on 600g)	Remarks
1	N.A.	N.A.	501.4	83.6	Mass of discarded material not recorded.
2	N.A.	N.A	501.2	83.5	Medium violent reaction
3	N.A.	N.A.	517.2	86.2	Calmer than reactions 1 and 2
4	N.A.	N.A.	511.6	85.3	Normal (calm) reaction
5	N.A.	N.A.	516	86	Normal reaction
6	535.9	89.3	525	87.5	Mass of discard recorded from this batch
7	528.7	88.1	510.4	85.1	Medium violent reaction
8	525.8	87.6	449.3	74.9	Excess material discarded around wire (75 grams) due to unclear region of wire
9	530	88.3	506.3	84.4	Medium violent reaction
10	391.4	65.2	368	61.3	Very violent reaction due to moisture and high relative humidity (71%)
11	336	56	317	52.8	Extremely violent reaction
12	268	44.7	248	41.3	Wet Mg caused very violent reaction
13	341	56.8	329	54.8	Violence comparable to #12
14	315	52.5	300	50	Extremely violent reaction
15	569.1	94.85	540.9	90.15	New batches of all reactants used. All powders were dry and sealed. Reaction was very calm (less violent than #s 1 to 9).
16	538.6	89.8	520.2	86.7	Calm reaction (normal)
17	553.9	92.3	537.8	89.6	Normal reaction (observed by Paul Sykes)
18	545.6	90.9	526.6	87.8	Normal reaction
19	514.3	85.7	495	82.5	Medium violent reaction

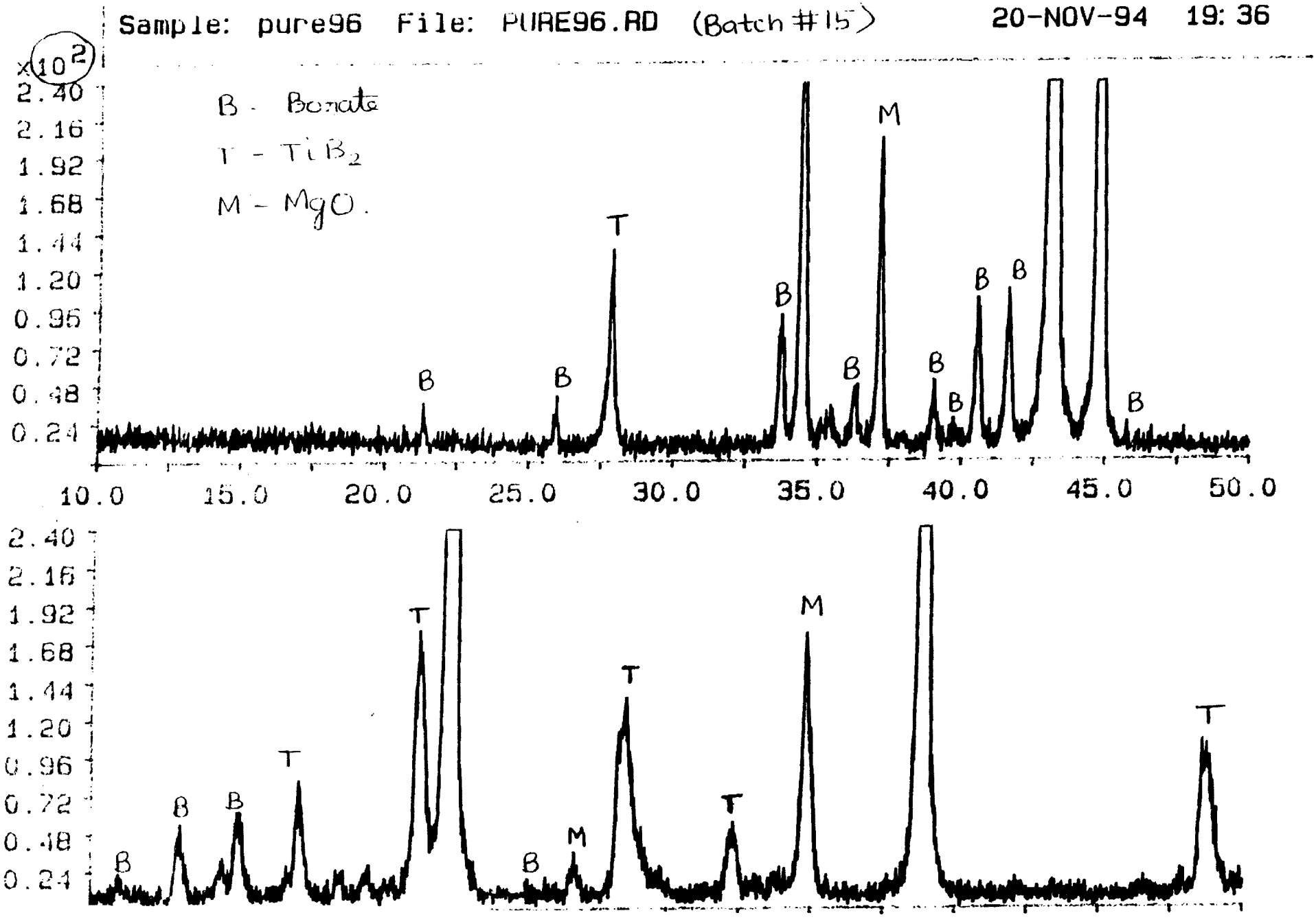
20	529.4	88.2	509.3	84.9	Medium violent reaction
21	523.5	87.25	501.7	83.6	Medium violent reaction. Relative humidity for #20 and 21 was 50% as compared to about 38% for #18 and 19
22	533.2	88.9	517.2	86.2	Normal reaction
23	538.8	89.8	532.8	88.8	Less discard (6 gm) due to wire being intact
24	551.7	92	538.7	89.8	Normal reaction
25	549	91.5	535	89.2	Normal reaction
26	544.5	90.8	527.5	87.9	Normal reaction
27	555.7	92.6	537.2	89.5	Normal reaction

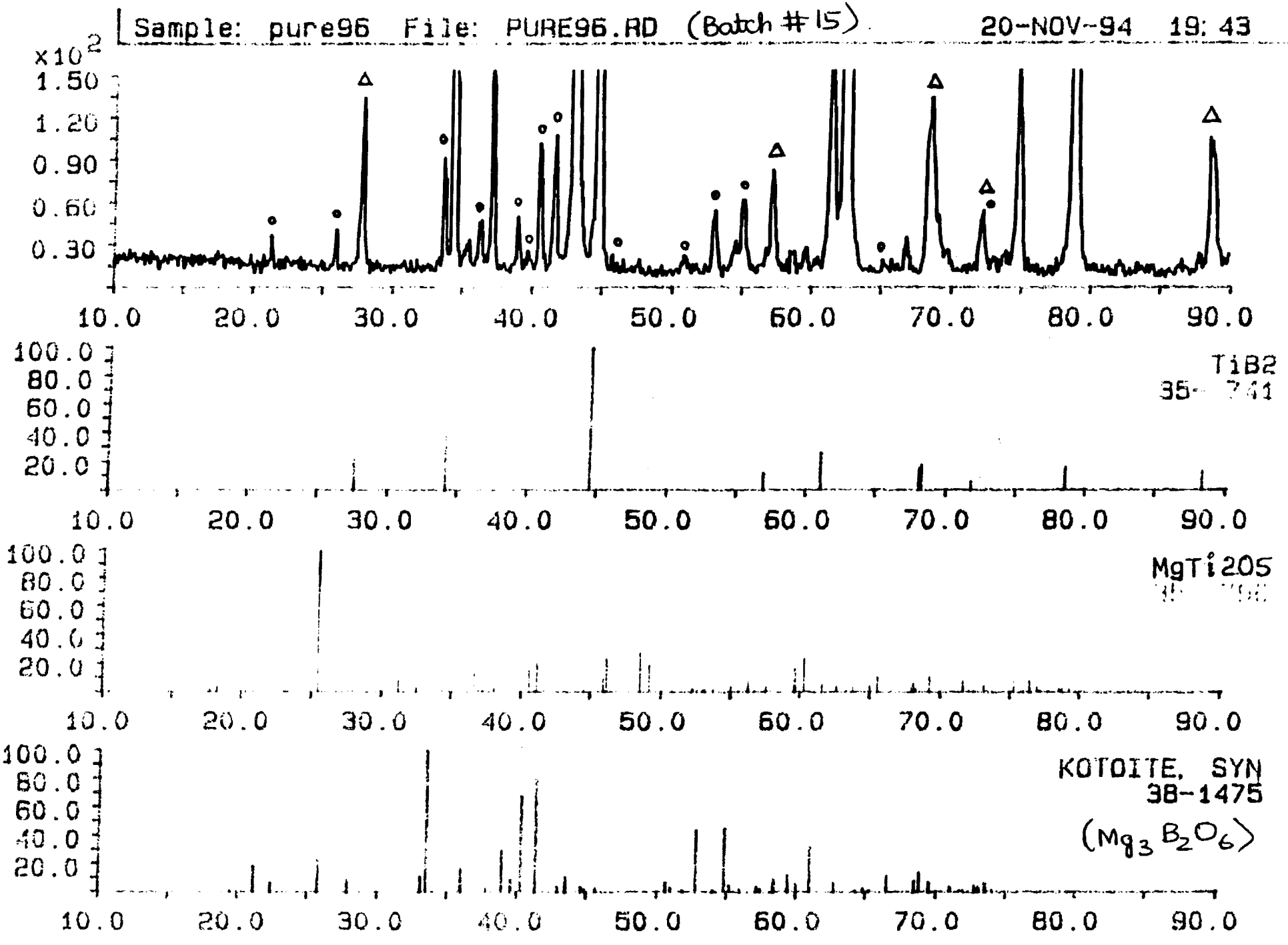

Sample: pure #95a File: PURE95.RD (Batch # 14) 20-NOV-94 19: 48
2.00
1.60
1.20
0.80
0.40
0.20
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0


Sample: pure #95a File: PURE95.RD (Batch #14) 20-NOV-94 19:58
10^2
B – Borate
T – TiB_2
M – MgO
B
T
M


Sample: pure #950 File: PURE95.RD (Batch#14) 20-NOV-94 20:02
△ TiB2
• Borate
10.0 30.0 50.0 70.0 90.0
TiB2
35- 741
MgTi2O5
35- 796
KOTOITE, syn
(Mg3B2O6)


Sample: pure96 File: PURE96.RD (Batch #15) 20-NOV-94 19:31
x10 3
2.40
2.16
1.92
1.68
1.44
1.20
0.96
0.72
0.48
0.24
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
2.40
2.16
1.92
1.68
1.44
1.20
0.96
0.72
0.48
0.24
50.0
55.0
60.0
65.0
70.0
75.0
80.0
85.0
90.0


Sample: pure96 File: PURE96.RD (Batch #15) 20-NOV-94 19:36
x(10^2)
2.40
2.16
1.92
1.68
1.44
1.20
0.96
0.72
0.48
0.24
B - Borate
T - TiB2
M - MgO.
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0


Sample: pure96 File: PURE96.RD (Batch #15) 20-NOV-94 19:43
x10 2
1.50
1.20
0.90
0.60
0.30
10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0
100.0
80.0
60.0
40.0
20.0
TiB2
35-741
MgTi2O5
KOTOITE, SYN
38-1475
(Mg3B2O6)

AEM Project 9815
11/7-11/11

A. Out of 40 lbs of composite on hand there is 7.5 lbs of ball milled powder.

B. There have been 6 Pure reactions completed. The last four were very violent. Two of them lost 50-75% of there volume because of this. These happened the 10th and the 11th, during and after the rain. It was discovered that we were using an older can of Magnesium. Friday afternoon a brand new 50# can of Mg was transferred to smaller cans for production. This should help the reactions immensely. A new . . .

C. The first hot press run started well but ended with a failed die punch. The punch collapsed after the line pressure was increased from 2200 psi to 2400 psi. It is assumed that the punch that failed was a low strength graphite material, all of the punches used now are new high strength graphite. The temperature was maintained at 1500 C throughout the trial. The sample was pressed to 91.5% dense with a density of 3.79 g/cm3. The resulting disk had a thickness of 0.545" with 0.500" being the desired thickness. New and stronger die punches have been machined and will be used Monday. The thermocouples have been repaired and were on line as of Friday afternoon. New connecters were purchased and installed. A new way of sealing the wire with silica has been installed and the results will be apparent after 5-6 runs. This 50 kw/10khz hot press has not been used in the past for TiB2 or composite TiB2/Al2O3 powder. As a result the parameters, such as temperature and pressure, have not been optimized yet.

D. The vacuum furnace has had the door seal replaced and another leak test was performed. The problem is not a leak. Geoving Gerard is testing the pump over the weekend to see if it will work. If it does not work we will remove the crucibles and see if they are containing too much moisture. This destroys the efficiency of the pump.

E. There is enough material on hand now to produce 40 lb of TiB2 powder and 30 lb of composite powder. All necessary orders have been placed for the hot pressing of the powders. We need to know if AEM will approve additional funding for more materials and supplies (e.g. 3" graphite punches, thermocouples, thermocouple tubes, pyrographite, etc.). Back-up supplies are necessary to prevent time delays.

2 purple (2#ea)
Post Co-op announce (Failed)
BOA → task
Keep inventory ↑ 25#

Other tasks:
Pan
Rearrangement
Material type
powder
T disk
T/A plus

KVL

Weekly report Venkatesh Sundaram
(week of 10/31 - 11/7)

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(1) AEM (Union Process) samples

Since the sample from AEM run #1(WC arms - 2 hours) was analyzed as being contaminated with tungsten carbide (WC) particles, the sample from run #2 (WC arms - 45 minutes) was analyzed using SEM/EDS. The sample preparation method has been described in detail in an earlier report (dated 10/24). The backscatter detector was inserted and the backscatter mode was used to detect the presence of WC particles. The micrographs of the backscatter image at 10k X. are attached. It is observed that the WC particles in this sample are much larger than those in the earlier sample (#1 - 2 hours). Random fields of view were chosen at 5000 X. and the number of particles were counted. Approximately 2-3 particles were found on an average per field of view. This is substantially higher than the ratio observed in the 2 hour sample. The reason for this could be that the particles are reduced in size when they are milled for 2 hours and some of the fine particles might not have been visible in the BSE image of sample #1 at 5000 X.

Run #2 (WC arms - 45 minutes)		Run #1 (WC arms - 2 hours)
# of fields of view = 10	(at 5000 X.)	# of fields of view = 25
# of WC particles = 22		# of WC particles = 8

Area of field of view = 20μm x 30μm.

EDS scans were acquired for the sample by placing the spot on a suspected WC particle. The results from the EDS are also attached. The tungsten peaks in the scan appear enhanced because of spot EDS on a WC particle.

(2) Particle size analysis

The samples from milling (Union Process) using WC and tool steel arms had to be analyzed for particle size. The Microtrac laser analyzer in MSE is yet to be fixed and it could take up to a month to be operational again. Meanwhile the second module with a particle size range of 0.6μm - 700μm has been attached to the system, but it has been decided to look for alternate machines for particle size determination.

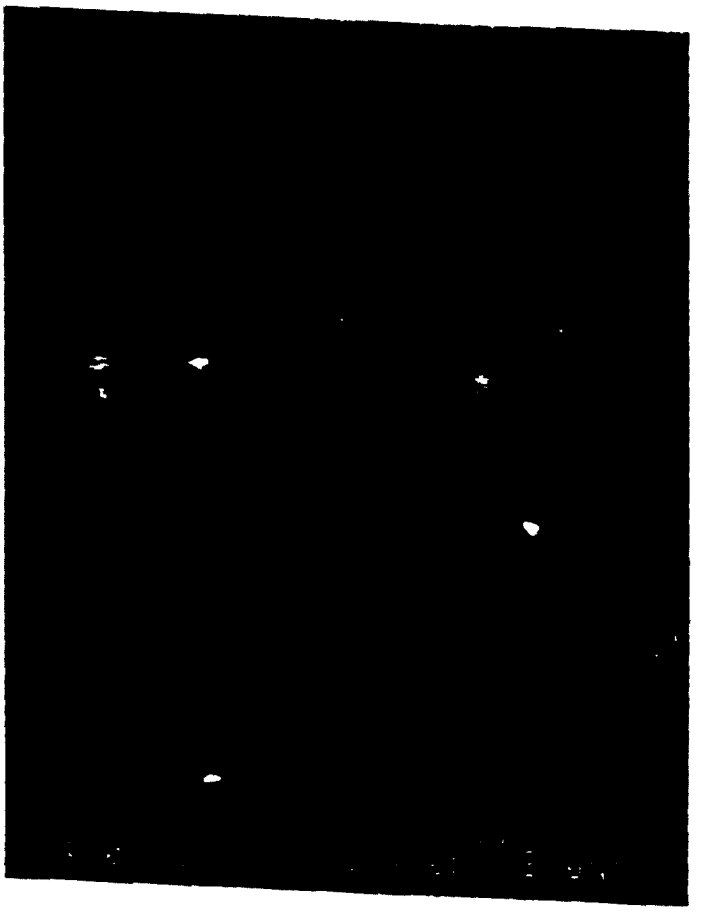
(3) X-ray diffraction of 600 gm batch sample (second batch of 600g composite)

A second batch of 600gm composite was made by Charles. XRD was done for this sample. The sample was prepared by using the small mill in room 269, Baker. The scan rate used was 1^0/minute. The output from the XRD is attached. It is observed that the extra peak which was

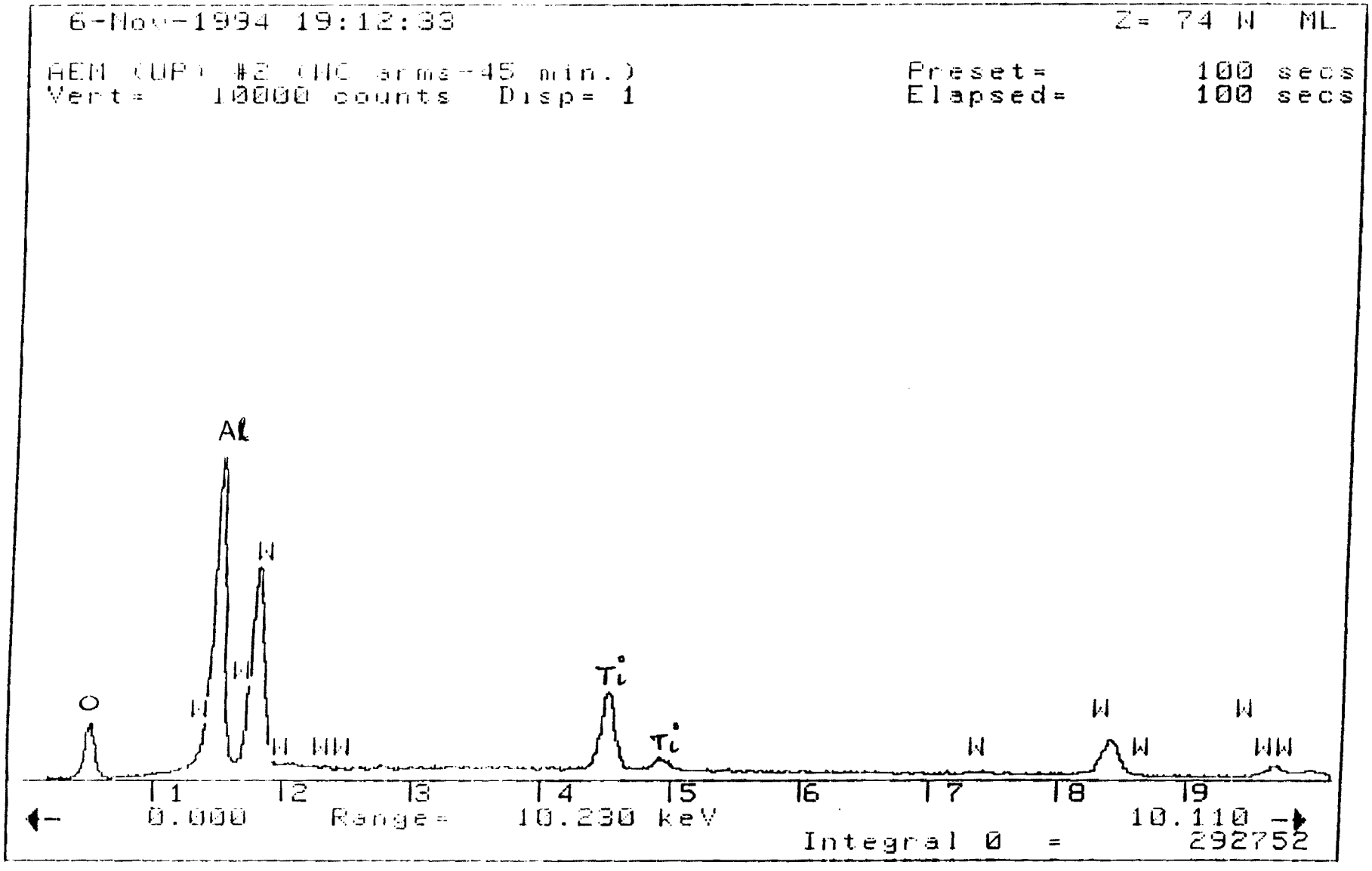
present in the first 600gm batch is still present in the trace. The peak matches with the strongest peak of Aluminum Titanate.

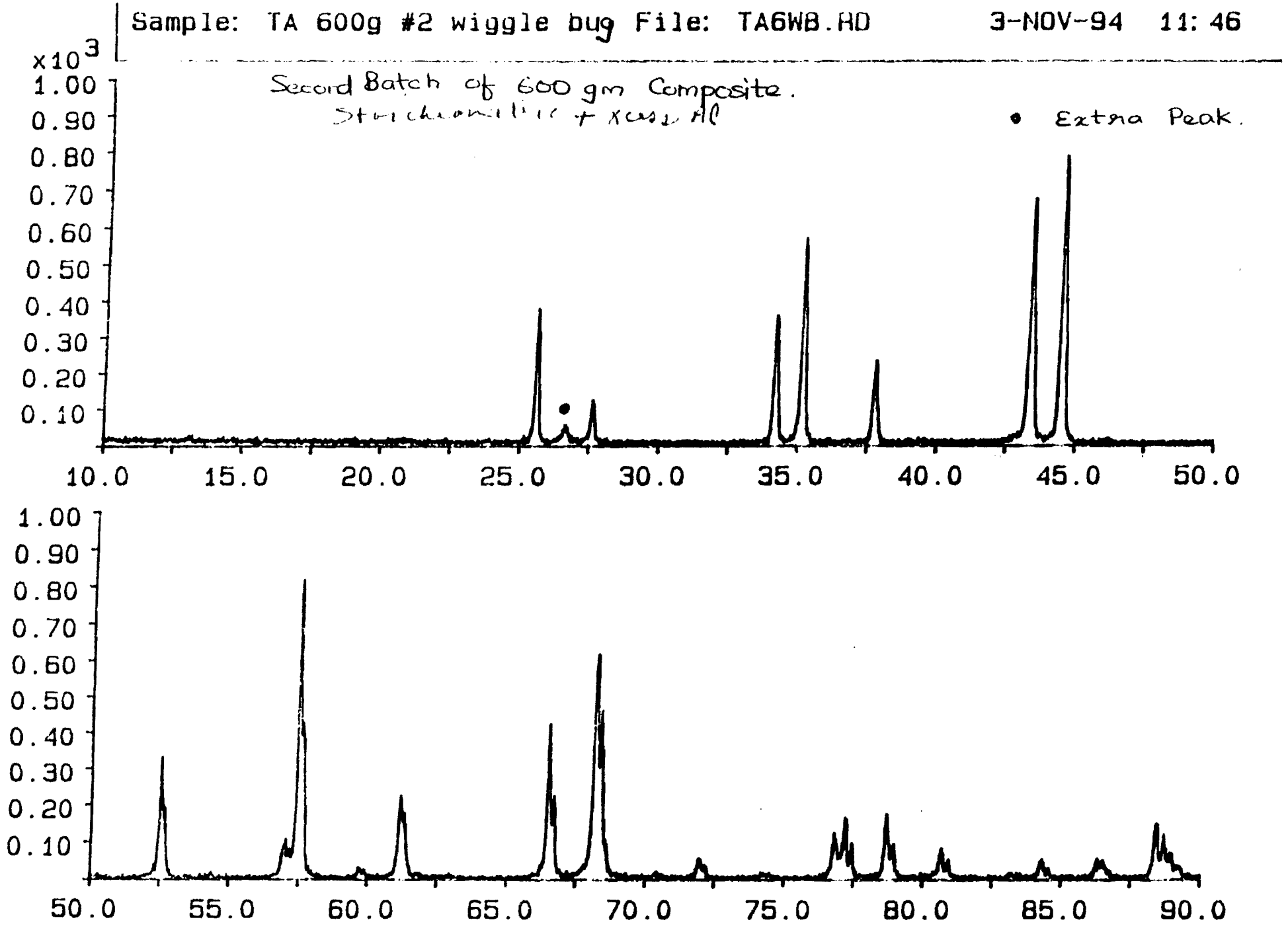
(4) Pure TiB_2 : XRD results

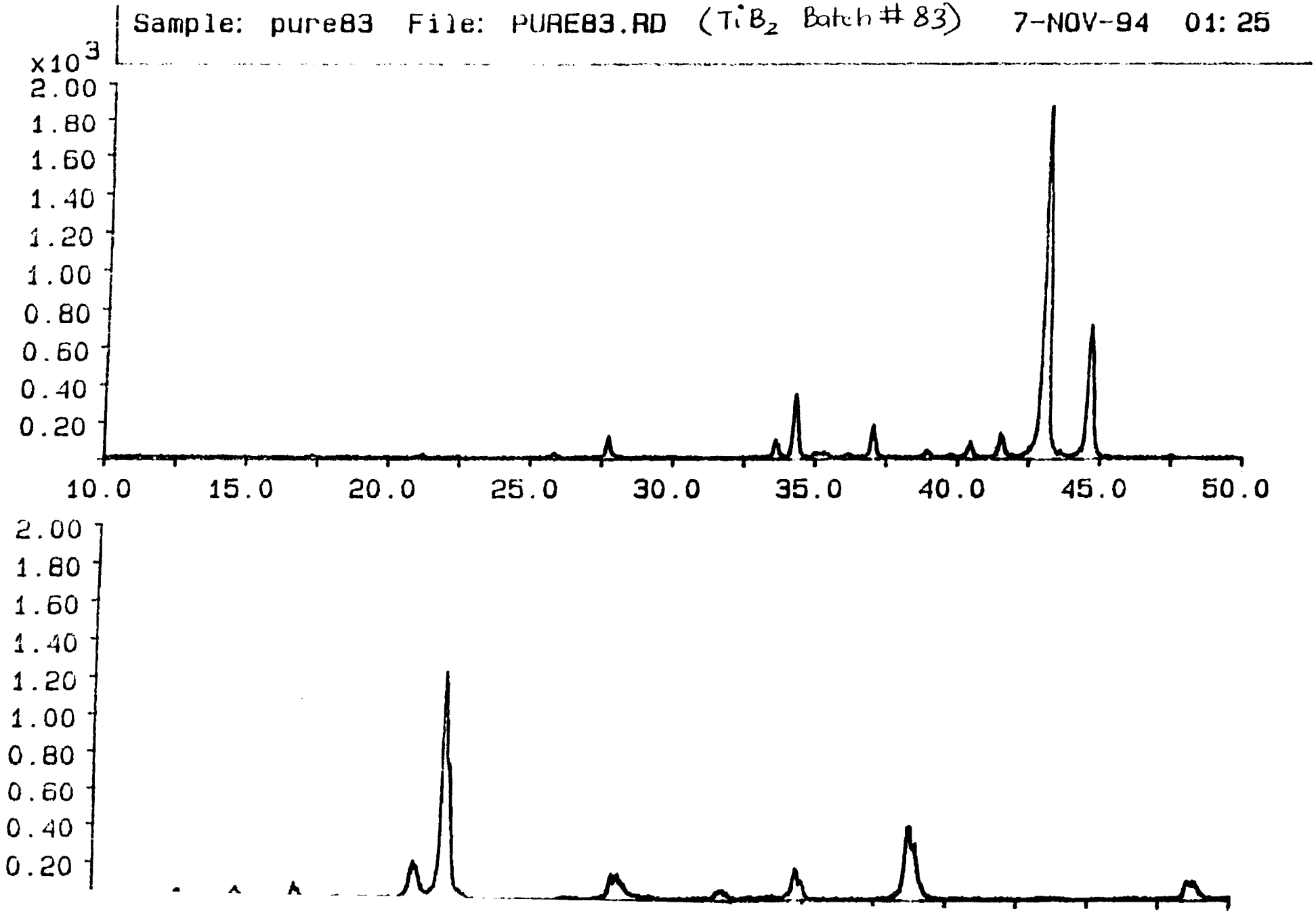
Samples were taken from the first two batches of the pure TiB_2. The reaction product could be ground in a mortar easily to from fine powder. Powder compact specimens were prepared fro x-ray diffraction. The scan rate used was about 1^0 / minute. The results from the XRD are attached. The two samples analyzed were from batch #83 and batch #84 (notebook 2). The patterns obtained indicate the presence of MgO (PDF #4-829) and TiB_2 (PDF #35-741). Minor amounts of magnesium titanate (PDF #35-792) and magnesium borate (PDF #38-1475) are also present in the sample.

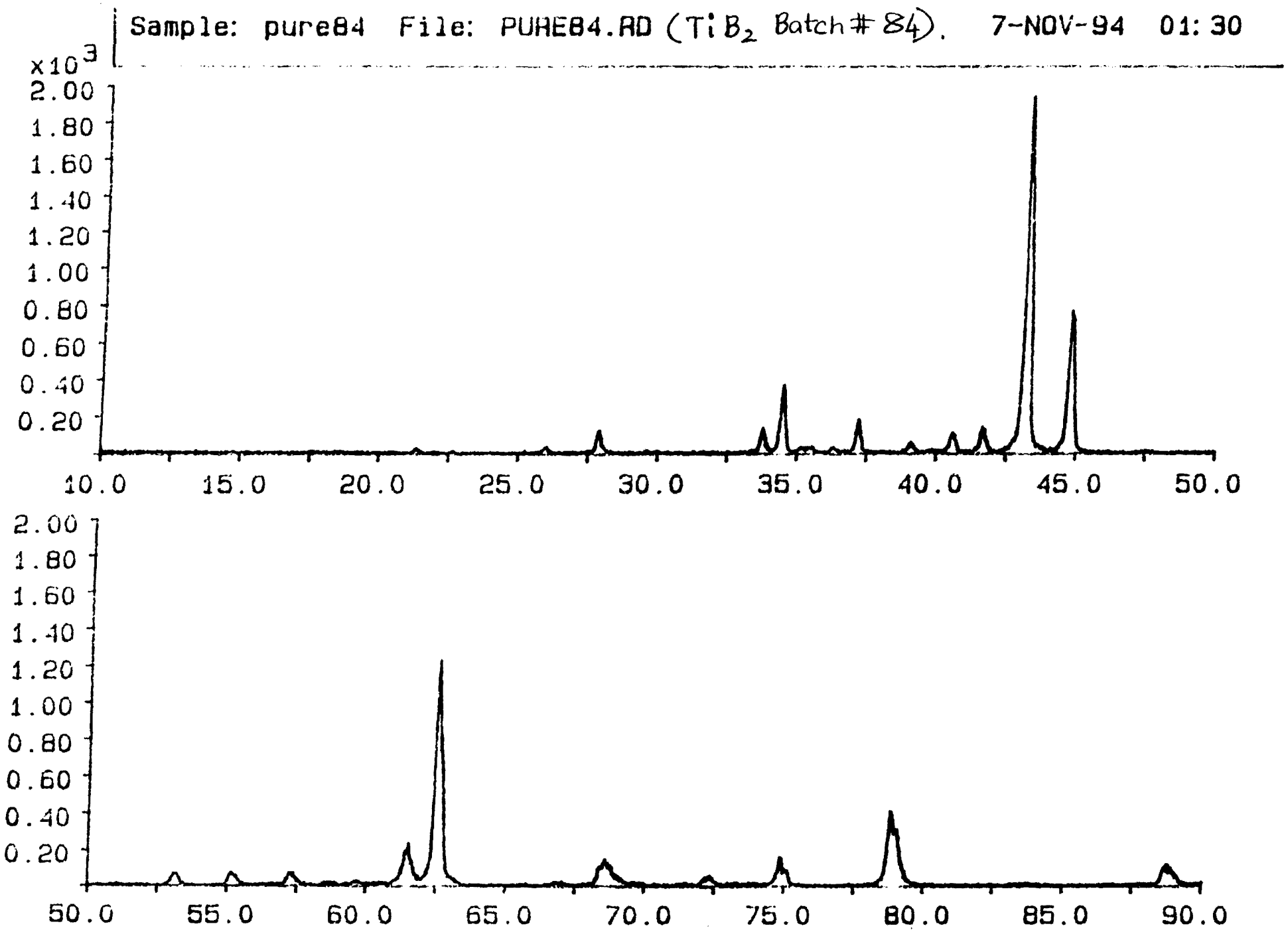


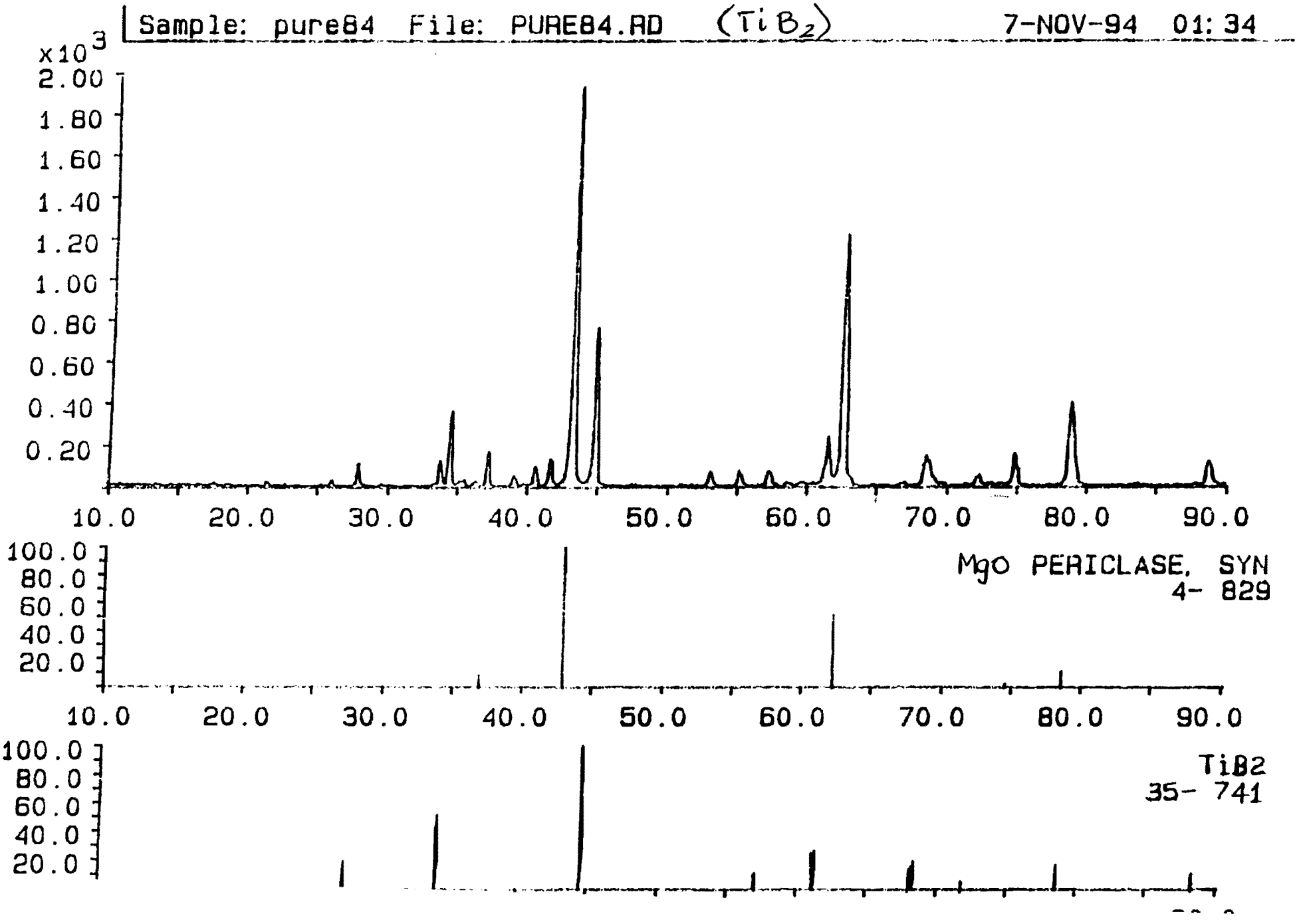
15 kV

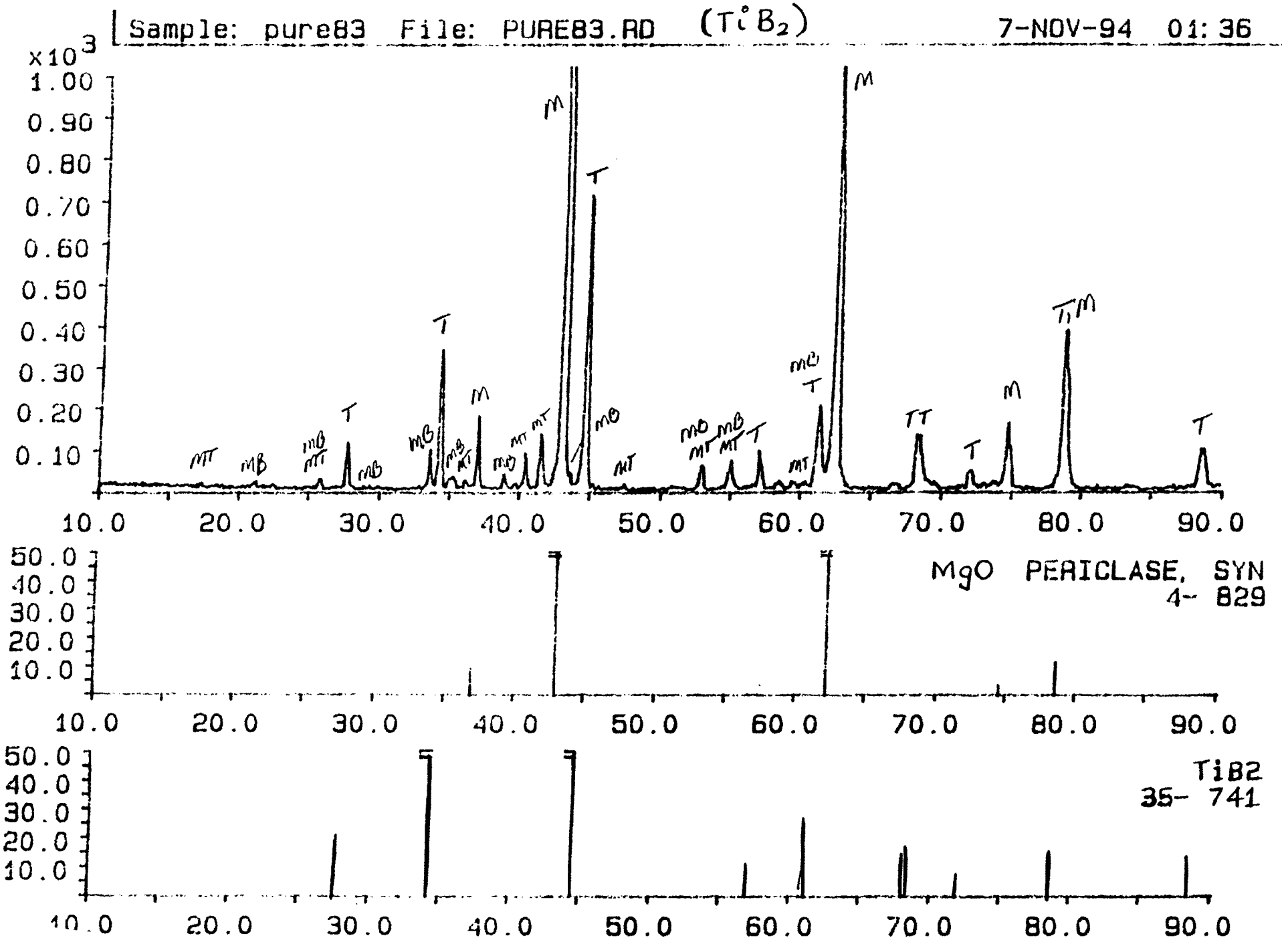

6-Nov-1994 19:12:33
Z= 74 N ML
AEM (UP) #2 (INC arms-45 min.)
Vert= 10000 counts Disp= 1
Preset= 100 secs
Elapsed= 100 secs
Al
O
Ti
Ti
1
2
3
4
5
6
7
8
9
0.000
Range= 10.230 keV
10.110
Integral 0 = 292752

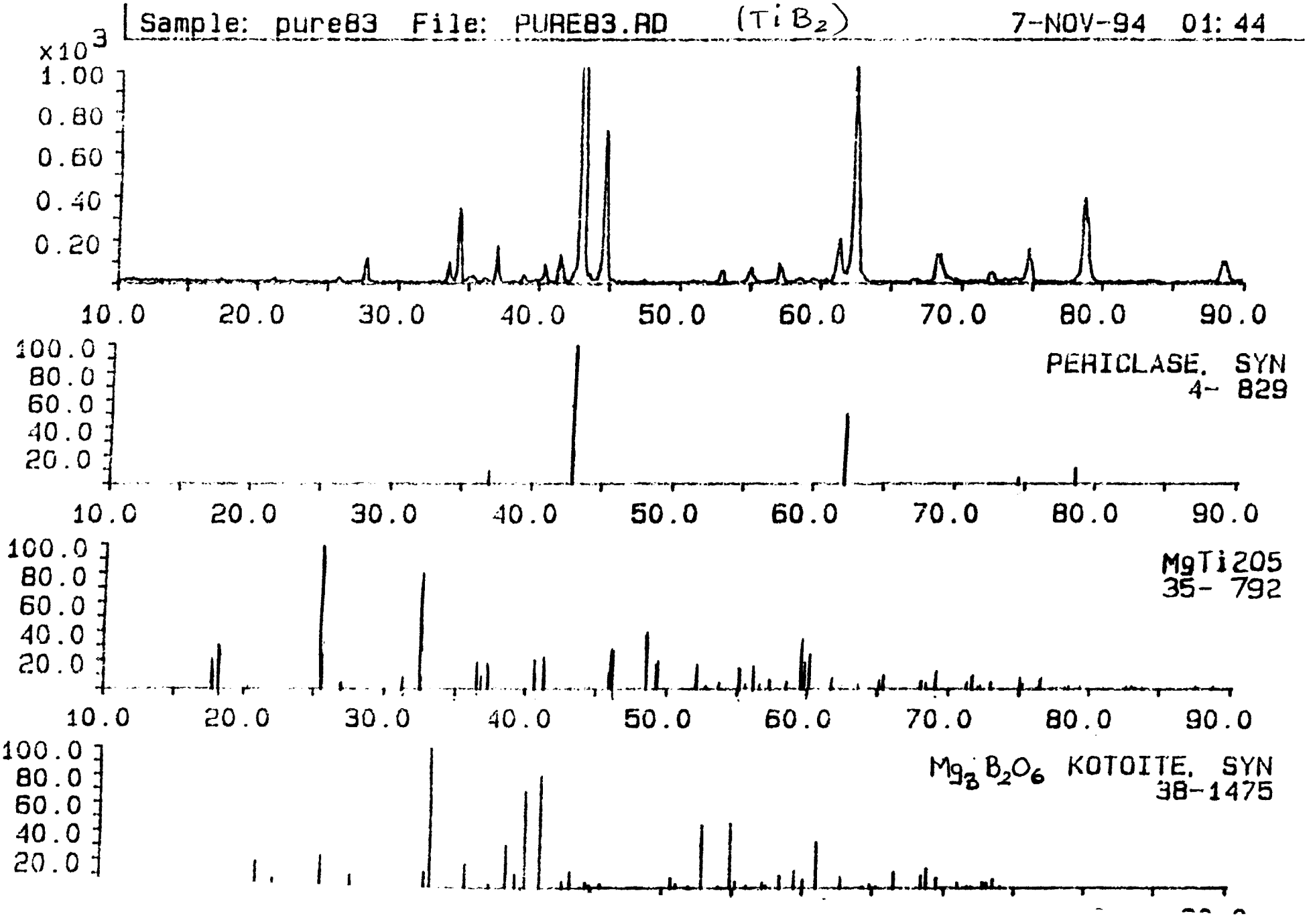

Sample: TA 600g #2 wiggle bug File: TA6WB.HD 3-NOV-94 11:46
x10^3
Second Batch of 600 gm Composite.
Stoichiometric + Xcess Al
• Extra Peak.
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
10.0 15.0 20.0 25.0 30.0 35.0 40.0 45.0 50.0
50.0 55.0 60.0 65.0 70.0 75.0 80.0 85.0 90.0


Sample: pure83 File: PURE83.RD (TiB_2 Batch # 83) 7-NOV-94 01:25
x10 3
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20


Sample: pure84 File: PUHE84.RD (TiB_2 Batch # 84). 7-NOV-94 01:30
x10^3
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
50.0
55.0
60.0
65.0
70.0
75.0
80.0
85.0
90.0


Sample: pure84 File: PURE84.RD (TiB_2) 7-NOV-94 01:34
x10 3
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
80.0
60.0
40.0
20.0
MgO PERICLASE, SYN
4- 829
TiB2
35- 741


Sample: pure83 File: PURE83.RD (TiB_2) 7-NOV-94 01:36
x10 3
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
MgO PERICLASE, SYN
4- 829
50.0
40.0
30.0
20.0
10.0
TiB2
35- 741


Sample: pure83 File: PURE83.RD (TiB_2) 7-NOV-94 01:44
x10 3
1.00
0.80
0.60
0.40
0.20
10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0
100.0
80.0
60.0
40.0
20.0
PERICLASE, SYN
4- 829
MgTi2O5
35- 792
$Mg_3B_2O_6$ KOTOITE, SYN
38-1475

AEM Project A-9859
11/21-11/23

A. The production of Pure TiB2 powder is reported in the attached report written by Venkatesh Sundaram.

B. All of the supplies needed to start leaching have been obtained. Leaching is still being held up by the lack of fume hoods. Back-up supplies have been tabulated and will be ordered to insure against set backs in case of any break downs in equipment.

C. Exactly five (5) pounds of unleached unmilled TiB2 powder was sent to Union Process more processing. There are two batches of 2 lbs. of composite ball mill ready to give to AEM. There have been 8 batches of pure powder ball milled. Each batch was ball milled separately for 30 minutes in a steel ball mill with 1/2 inch steel balls. The result is a very fine black powder as opposed to grey in the composite.

D. Each of the composite disks were polished and checked again for their densities. Disk number two came out with a density of 3.720 g/cm3 for a percent dense of 89.85%. Disk number three came out with a density of 3.929 g/cm3 for a percent dense of 94.91%. One hundred percent dense is 4.14 g/cm3. On the next hot press run we will try raising the temperature faster and go up to 1575 C. The pressure has maximized at 2890 psi (line pressure).

E. There have been 4 containers of TiO2 recieved from SCM Chemicals of Baltimore, MD. wt ?

F. There have been 2 containers of 60 mesh B2O3 recieved from US Borax. wt ?

COMPOSITE DISK DATA

DISK	MASS-GRO	MASS-NE	DENSIT	% DENS	TEMP-	PRESSU	TIME
1	238.5		3.79	91.55	1500	2400	2.16
2	238.2	238.13	3.72	89.86	1500	2800	3.17
3	239.8	233.79	3.929	94.90	1525	2890	2.25
4				0.00			
5				0.00			
6				0.00			

PURE BALL MILLING

	MASS-GROSS	MASS NET	% LOSS
6	525	520.8	99.20
7	510.4	509.6	99.84
8	449.3	438.5	97.60
9	506.3	495.2	97.81
10	368	366.7	99.65
11	317	314.8	99.31
12	248	232.9	93.91
13	329		
14			

AEM Project #A9815 (Pure TiB_2)
Weekly report
(week of 11/21 - 11/23)

Alison Carney
Venkatesh Sundaram

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(1) During the last week, a total of 5 pure TiB_2 reactions were performed yielding 5.4 pounds of powder. So far, a total of 32 reactions have been completed yielding a total amount of 33.9 lb. of powder mixture ($MgO+TiB_2$). A detailed table of all the reactions is attached.

As suggested in last week's meeting, the crucibles were weighed after each step in the synthesis process. This was done for three batches (#29, 30 and 31). A detailed table of weights is attached. Also, it was suggested that the bottom crucibles should not be cleaned completely before reusing. The crucibles from the batches done last week have built up a layer of the reaction product at the bottom and sides. This should prevent any contamination from the silica crucible and also aid in easier removal of the product from the crucibles. Due to this build-up, the yields from the last few batches are reduced. It is expected that after a complete layer of product is formed inside the crucibles, the yield will increase significantly. It has been decided that the weighing of the crucibles will be done after a few reactions to check for the higher yield.

(2) A total of 5 lb. of pure powder were given to AEM last week. These were from the batches #1 to #5. Also, 2 lb. of the 8 hour ball milled composite powder was given from batches # 45 to 50 (composite). In addition to this, two samples, one from the ball milled composite and one from the pure product, each weighing 20 grams were given for display purposes.

(3) The product from the pure TiB_2 reaction was ball milled in a steel mill with 1/2 inch steel balls for 30 minutes. A total of 8 batches (#6 to #13) were milled last week. Charles will give more details about this operation.

Type B ~ (Type S now)
1. Venky
a. 2nd type dist
1. TiB_2/MgO ~
2. " " Ball Milled

Hot Press
1500 psi unit →
1525 C

Batch #	Mass obtained (grams) (after reaction)	Yield (%) (after reaction)	Mass obtained (grams) (after bottling)	Yield (%) (based on 600g)	Remarks
1	N.A.	N.A.	501.4	83.6	Mass of discarded material not recorded.
2	N.A.	N.A.	501.2	83.5	Medium violent reaction
3	N.A.	N.A.	517.2	86.2	Calmer than reactions 1 and 2
4	N.A.	N.A.	511.6	85.3	Normal (calm) reaction
5	N.A.	N.A.	516	86	Normal reaction
6	535.9	89.3	525	87.5	Mass of discard recorded from this batch
7	528.7	88.1	510.4	85.1	Medium violent reaction
8	525.8	87.6	449.3	74.9	Excess material discarded around wire (75 grams) due to unclear region of wire
9	530	88.3	506.3	84.4	Medium violent reaction
10	391.4	65.2	368	61.3	Very violent reaction due to moisture and high relative humidity (71%)
11	336	56	317	52.8	Extremely violent reaction
12	268	44.7	248	41.3	Wet Mg caused very violent reaction
13	341	56.8	329	54.8	Violence comparable to #12
14	315	52.5	300	50	Extremely violent reaction
15	569.1	94.85	540.9	90.15	New batches of all reactants used. All powders were dry and sealed. Reaction was very calm (less violent than #s 1 to 9).
16	538.6	89.8	520.2	86.7	Calm reaction (normal)
17	553.9	92.3	537.8	89.6	Normal reaction (observed by Paul Sykes)
18	545.6	90.9	526.6	87.8	Normal reaction
19	514.3	85.7	495	82.5	Medium violent reaction

20	529.4	88.2	509.3	84.9	Medium violent reaction
21	523.5	87.25	501.7	83.6	Medium violent reaction. Relative humidity for #20 and 21 was 50% as compared to about 38% for #18 and 19
22	533.2	88.9	517.2	86.2	Normal reaction
23	538.8	89.8	532.8	88.8	Less discard (6 gm) due to wire being intact
24	551.7	92	538.7	89.8	Normal reaction
25	549	91.5	535	89.2	Normal reaction
26	544.5	90.8	527.5	87.9	Normal reaction
27	555.7	92.6	537.2	89.5	Normal reaction
28	528.4	88.1	514.5	85.75	Normal reaction
29	475	79.2	465	77.5	It was decided to build up a layer of reaction product in the crucible to avoid silica contamination and to increase yield. Hence, the lower yields in the next few batches.
30	495.1	82.5	487	81.2	Normal reaction
31	502.5	83.75	492.6	82.1	Medium violent reaction
32	489	81.5	478.8	79.8	Medium violent reaction

***Table*: Detailed listing of weights measured after each step in the synthesis process.**

(1) Batch #29

Top crucible	Before reaction	1519.5 g	Gain in weight = 22.7 g
	After reaction	1542.2 g	
Bottom Crucible	At the start	1757.7 g	Weight of powder = 598.7 g (99.8%)
	After sifting	2356.4 g	
	After reaction	2349.6 g	Total discard = 13.6 g
	After discard	2336.0 g	Difference in weight before and after bottling = 465 g
	After bottling	1871.0 g	Weight gained by bottom = 113.3 g

Note: (1) Least count of balance used = 0.1 lb.
Conversion factor: 1 lb. = 453.59 g.

(2) Weight gained by the metal weight placed on top of the crucibles = 1.5 grams

Discarded material = 10 g
Weight of the discarded wires = 3.6 g

Weight of powder bottled = 465 g

Net weight gained by top and bottom crucibles + discard = 113.3 + 1.5 + 10 + 22.7
= 147.5 g
Weight of powder lost during synthesis process = 600 - 465 = 135 g

The additional weight gain may be due to the inaccuracy in measuring weights and due to the pick up of oxygen from the atmosphere during the reaction.

(2) Batch #30

Top crucible	Before reaction	1417.5 g	Gain in weight = 15.8 g
	After reaction	1433.3 g	
Bottom Crucible	At the start	1642 g	Weight of powder = 598.7 g (99.8%)
	After sifting	2240.7 g	
	After reaction	2238.5 g	Total discard = 6.8 g
	After discard	2231.7 g	Difference in weight before and after bottling = 489.9 g
	After bottling	1741.8 g	Weight gained by bottom = 99.8 g

Note: (1) Least count of balance used = 0.1 lb.
Conversion factor: 1 lb. = 453.59 g.

(2) Weight gained by the metal weight placed on top of the crucibles = 1.5 grams

Discarded material = 8.1 g

Weight of powder bottled = 487 g

Net weight gained by top and bottom crucibles + discard = 99.8 + 1.5 + 8.1 + 15.8
= 125.2 g

Weight of powder lost during synthesis process = 600 - 487 = 113 g

The additional weight gain may be due to the inaccuracy in measuring weights and due to the pick up of oxygen from the atmosphere during the reaction.

(3) Batch #31

Top crucible	Before reaction	1537.7 g	Gain in weight = 18.1 g
	After reaction	1555.8 g	
Bottom Crucible	At the start	1864.3 g	Weight of powder = 600 g (100%)
	After sifting	2465.3 g	
	After reaction	2458.5 g	Total discard = 13.65 g
	After discard	2444.85 g	Difference in weight before and after bottling = 494.45 g
	After bottling	1950.4 g	Weight gained by bottom = 86.1 g

Note: (1) Least count of balance used = 0.1 lb.
Conversion factor: 1 lb. = 453.59 g.

(2) Weight gained by the metal weight placed on top of the crucibles = 1.5 grams

Discarded material = 9.9 g
Weight of the discarded wires = 3.75 g

Weight of powder bottled = 492.6 g

Net weight gained by top and bottom crucibles + discard = 86.1 + 1.5 + 9.9 + 18.1
= 115.6 g
Weight of powder lost during synthesis process = 600 - 492.6 = 107.4 g

The additional weight gain may be due to the inaccuracy in measuring weights and due to the pick up of oxygen from the atmosphere during the reaction.

AEM Project A-9859
11/28-12/2

A. The fourth hot press run was completed on Wednesday. The travel indicator was jammed so the run was timed to have a similar soak time to the third run. The temperature was increased to 1580 C for this run and the pressure was kept constant at 2890 line psi. 2890 psi is the maximum safe pressure for the grade graphite we are using. The soak time was stopped at one hour and thirty five minutes. This run resulted in a disk with a mass of 233.5 and a percent density of 97.59%. This was measured after the disk was polished with a diamond polishing disk.

B. There have been 42 Pure reactions run for a total of 40 pounds of unleached powder. See Vekatesh's report for details.

C. The fume hoods in 108 78H, Area II are all broken and will require a repair costing $7200.00. The leaching will be temporarily moved to room 118 in the Baker building. All of the necessary equipment has been acquired or ordered from Fischer. The PH probes and other supplies needed will be picked up on Monday December 5.

D. There has been several containers of sample materials received:

1) 4 containers of TiO2, 5 lbs each from SCE Chemicals.

2) 2 containers of 60 mesh and 2 containers of 4 mesh B2O3 from US Borax.

E. The milled powder sent from Union Process was received on Friday Dec. 2. There is approximately 6.5 pounds of 45 min. milled powder.

PURE POWDER INVENTORY

TOTAL

MASS G		MASS LB	
GROSS	NET	GROSS	NET
17644	19601	38.86	43.17

AVG G G		AVG LB	
GROSS	NET	GROSS	NET
504.12	490.02	1.11	1.08

AVG %	
GROSS	NET
84.02	81.67

COMPOSITE POWDER INVENTORY

POWDER

	MASS-G	MASS-LB
UNMILLE	12418.00	27.35
MILLED	3437.90	7.57
	15855.90	34.92

GIVEN TO AEM

UNMILLE		10507.8	23.14
MILLED	HR 8	80	0.18
	HR 15	85	0.19
	HR 30	75	0.17
	SAMP-12	180	0.40
	TOTAL	10927.8	24.07

RETURNED

MILLED			
MIN 10	955.5	2.10	
MIN 20	976.6	2.15	
MIN 45	903.9	1.99	
HR 2	931.5	2.05	
MIN 45	968.0	2.13	*
MIN 45	1052.8	2.32	*MASS WITH BAG*
MIN 45	966.5	2.13	*
TOTAL	6754.8	14.88	

TOTALS

PRODUC	28694.7	63.20	THIS DOES NOT INCLUDE BATCHES 2-9

HOT PRESS

PARAMETERS

RUN	TYPE POWDER	MASS {G}	DRY-PRESS {PSI}	FINAL-PRESS {PSI}	FINAL TEMP {C}	RAMP TIME {MIN}	SOAK TIME {HOURS}	THERMOCOUPLE TYPE
1	T/A COMP	240.0	3374	5399	1500	25	1:51	B
2	T/A COMP	239.7	3374	6298	1500	20	2:55	S
3	T/A COMP	239.8	3374	6501	1525	25	1:54	S
4	T/A COMP	239.9	3374	6501	1580	35	1:35	S

DISK DATA

DISK	DIMENSIONS DIAMETER {IN}	DIMENSIONS THICKNESS {AVG-IN}	GROSS MASS {G}	NET MASS {G}	THEORETICAL DENSITY {G/CM3}	TRUE DENSITY {G/CM3}	PERCENT DENSE
1	3	0.545	240.0	238.50	4.14	3.79	91.55
2	3.0465	0.55	239.7	238.13	4.14	3.72	89.86
3	3.039	0.512	239.8	233.79	4.14	3.93	94.93
4	3.041	0.495	239.9	233.50	4.14	4.04	97.58

For Dr. Logan.

AEM Project #A9815 (Pure TiB_2)
Weekly report
(week of 11/28 - 12/5)

Alison Carney
Venkatesh Sundaram

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(1) During the last week, a total of 13 pure TiB_2 reactions were performed yielding 14.95 pounds of powder. So far, a total of 45 reactions have been completed yielding a total amount of 48.85 lb. of powder mixture ($MgO+TiB_2$). A detailed table of all the reactions is attached.

In the last two weeks, the 7 sets of crucibles have been used allowing a residual layer of reaction product to build up inside the crucibles. Since the crucibles have been used in rotation, the yields from the reactions in the last two weeks vary considerably. After one more week of reactions, all the crucibles should have built up a complete layer of product and this will result in consistent and higher yields.

(2) The thermal insulation in the lid used during the pure TiB_2 reaction was completely replaced last week. It was observed that the flames were well contained within the lid in subsequent reactions.

(3) XRD of samples taken from the deposits

One sample each was taken from the white powder deposited on the side of the bottom crucible and from the hard crust which forms on the inner surface of the bottom crucible. These two samples were x-rayed to check for the constituent phases. The sample for the XRD was prepared by using double sided tape on a piece of glass slide. The powder was stuck on the tape and pasted to the slide. This slide was then placed in the sample holder and the surface was leveled using a frosted glass surface. For the crust sample, the hard material was ground in an alumina mortar before sample preparation. The scan rate used was about 1^0 / minute. The results are attached.

As suspected, the white powder deposit has been identified as MgO. The comparative plot for this sample is also attached. The crust sample contains MgO as well as Mg (PDF #4-770) and Mg_2Si (PDF #35-773). A comparative plot for this material is also attached.

(4) Smoke analysis

Samples from the smoke are being collected by fixing sample glass slides and SEM stubs with tape stuck on them on the exhaust fan. It has been observed that very less smoke escapes from the reactions due to the use of the lid. It is expected that required amounts of particulates from the smoke will accumulate in about two more weeks. These will then be analyzed using XRD and SEM.

(5) Particle Size Analysis

The Microtrac laser particle size analyzer is finally back to operating status. Some preliminary runs were done over the weekend after some effort in setting up the small particle analyzer (SPA). The medium used was distilled water and DARVAN No. 7 (sodium poly methacrylate) was used as dispersing agent. The powder was sampled by Coning & Quartering and then mixed in water containing three drops of Darvan. An ultrasonic dismembrator (Fisher model #300) was used to disperse the particles. One measurement consists of three 30 second runs and the average of the three runs is calculated.

There was a problem with the laser alignment in the Microtrac. This problem could not be fixed over the weekend and will be corrected on Monday (Dec. 5). The particle size analysis will be done this week and the complete particle size data for the ball milled composite powders and the pure powder mixture will be made available next week.

Batch #	Mass obtained (grams) (after reaction)	Yield (%) (after reaction)	Mass obtained (grams) (after bottling)	Yield (%) (based on 600g)	Remarks
1	N.A.	N.A.	501.4	83.6	Mass of discarded material not recorded.
2	N.A.	N.A.	501.2	83.5	Medium violent reaction
3	N.A.	N.A.	517.2	86.2	Calmer than reactions 1 and 2
4	N.A.	N.A.	511.6	85.3	Normal (calm) reaction
5	N.A.	N.A.	516	86	Normal reaction
6	535.9	89.3	525	87.5	Mass of discard recorded from this batch
7	528.7	88.1	510.4	85.1	Medium violent reaction
8	525.8	87.6	449.3	74.9	Excess material discarded around wire (75 grams) due to unclear region of wire
9	530	88.3	506.3	84.4	Medium violent reaction
10	391.4	65.2	368	61.3	Very violent reaction due to moisture and high relative humidity (71%)
11	336	56	317	52.8	Extremely violent reaction
12	268	44.7	248	41.3	Wet Mg caused very violent reaction
13	341	56.8	329	54.8	Violence comparable to #12
14	315	52.5	300	50	Extremely violent reaction
15	569.1	94.85	540.9	90.15	New batches of all reactants used. All powders were dry and sealed. Reaction was very calm (less violent than #s 1 to 9).
16	538.6	89.8	520.2	86.7	Calm reaction (normal)
17	553.9	92.3	537.8	89.6	Normal reaction (observed by Paul Sykes)
18	545.6	90.9	526.6	87.8	Normal reaction
19	514.3	85.7	495	82.5	Medium violent reaction

20	529.4	88.2	509.3	84.9	Medium violent reaction
21	523.5	87.25	501.7	83.6	Medium violent reaction. Relative humidity for #20 and 21 was 50% as compared to about 38% for #18 and 19
22	533.2	88.9	517.2	86.2	Normal reaction
23	538.8	89.8	532.8	88.8	Less discard (6 gm) due to wire being intact
24	551.7	92	538.7	89.8	Normal reaction
25	549	91.5	535	89.2	Normal reaction
26	544.5	90.8	527.5	87.9	Normal reaction
27	555.7	92.6	537.2	89.5	Normal reaction
28	528.4	88.1	514.5	85.75	Normal reaction
29	475	79.2	465	77.5	It was decided to build up a layer of reaction product in the crucible to avoid silica contamination and to increase yield. Hence, the lower yields in the next few batches.
30	495.1	82.5	487	81.2	Normal reaction
31	502.5	83.75	492.6	82.1	Medium violent reaction
32	489	81.5	478.8	79.8	Medium violent reaction
33	507.3	84.55	496	82.7	Medium violent reaction
34	495.6	82.6	488.6	81.4	Normal reaction
35	500	83.33	488.8	81.5	Violent reaction with a large "pop"

36	574.5	95.75	566.9	94.5	Medium violent reaction. Note that the last few and the next few reactions were done with different crucibles being reused with a buildup. Hence the variation in yields.
37	604.6	100.8	592.2	98.7	Normal reaction. The yield probably includes some material from the previous batch reacted in that crucible.
38	500.5	83.4	492.6	82.1	Normal reaction
39	520.4	86.7	514.6	85.8	Normal reaction
40	543.2	90.5	538.3	89.7	Normal reaction
41	563.45	93.9	537	89.5	New insulation in the lid. Medium violent reaction. Large discard.
42	511	85.2	504.8	84.1	Medium violent reaction
43	546	91	538	89.7	Normal reaction
44	533.4	88.9	524.1	87.35	Normal reaction
45	501.9	83.7	499.2	83.2	Medium violent reaction

TED PEAKS FILE 4-DEC-94 23:35

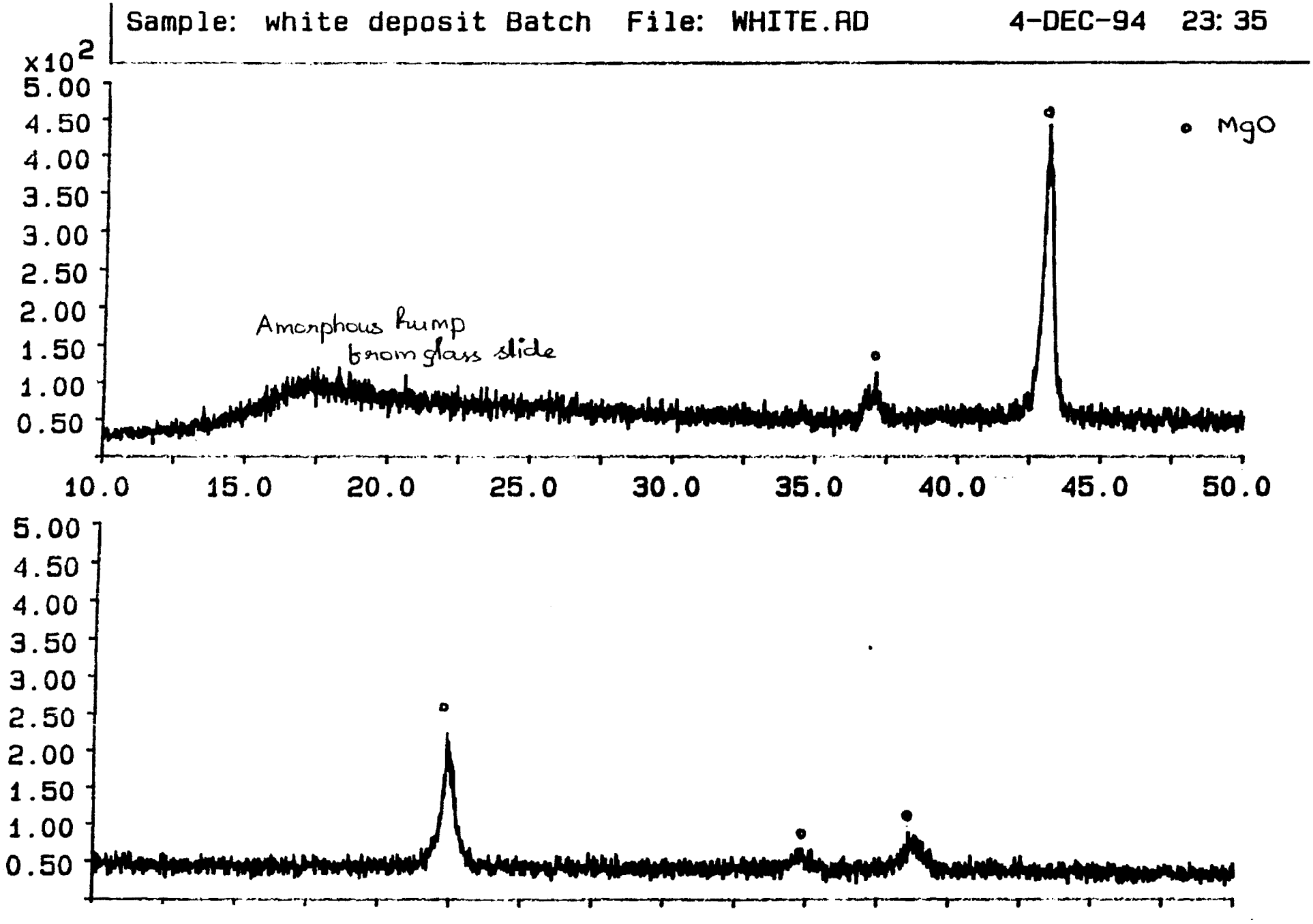
ith TAD

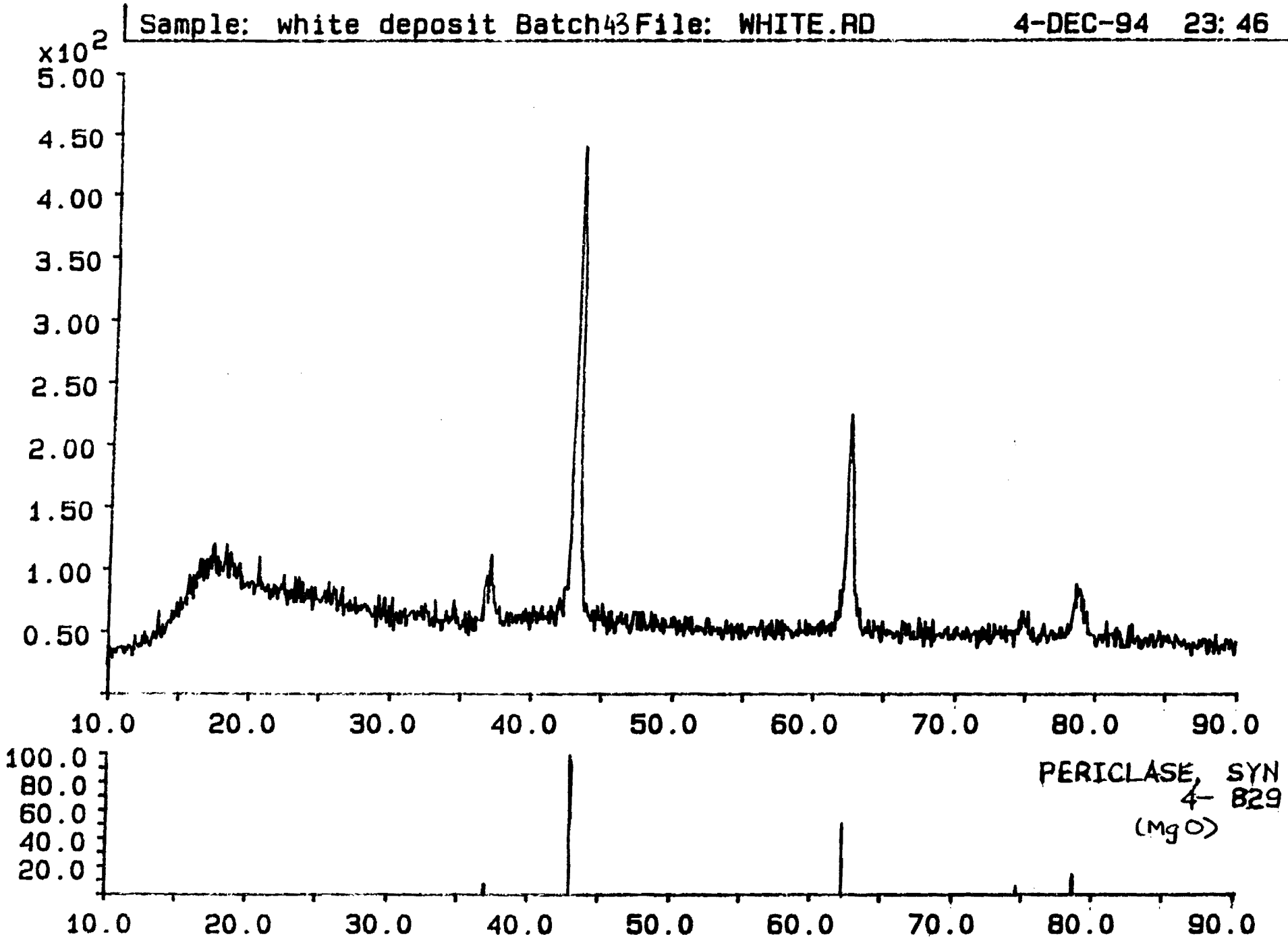
White Deposit.

d DI file name : WHITE.DI
nal data file name : WHITE.RD
.e identification : white deposit Batch# 43
urement date/time : 4-DEC-94 19:11
:actometer system : 1
:ator settings : 40 kV, 30 mA
lphal,2 wavelengths : 1.54060, 1.54439 Ang
size, sample time : 0.015 deg, 1.00 s, 0.015 deg/s
:hromator used : Yes
:gence slit : Automatic (Irradiated sample length: 10.0 mm)

ysis program number : 3
angle range : 10.000 - 90.010 deg
e in D spacing : 1.08927 - 8.8382 Ang
position criterion : Top of smoothed data
t peak width range : 0.00 - 2.00 deg
m peak significance : 1.00
er of peaks in file : 6 (Alphal: 6, Amorphous: 0)
mum intensity : 346. cts, 346.0 cps

Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D spac (Ang)	I/Imax (%)	Type A1	Type A2	Type Ot	Sign
16.9225	1.68	38.	53.	5.2351	11.11	X	X		3.09
37.0900	0.18	41.	44.	2.4220	11.84	X	X		1.32
43.0450	0.30	346.	49.	2.0997	100.00	X	X		12.30
62.4225	0.15	156.	37.	1.4865	45.16	X	X		1.41
74.7900	0.48	18.	37.	1.2684	5.10	X	X		1.12
78.7700	0.48	40.	34.	1.2140	11.47	X	X		3.09


Sample: white deposit Batch File: WHITE.AD 4-DEC-94 23:35
x10^2
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
MgO
Amorphous hump
from glass slide
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0


Sample: white deposit Batch43 File: WHITE.RD 4-DEC-94 23:46
x10 2
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
80.0
60.0
40.0
20.0
PERICLASE, SYN
4- 829
(MgO)

DETECTED PEAKS FILE 5-DEC-94 3:33

...D with TAD

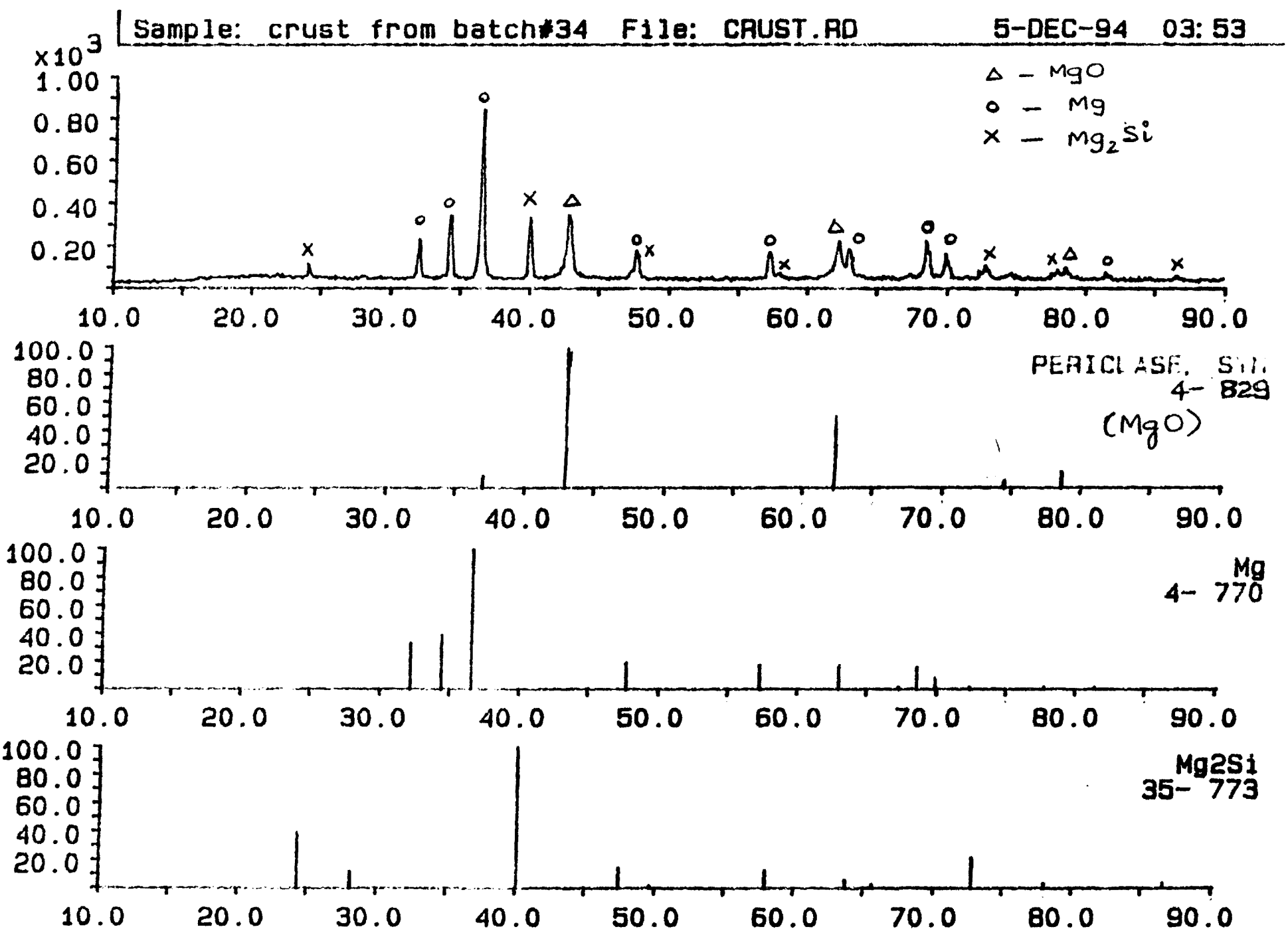
Hard crust.

Listed DI file name : CRUST.DI
Original data file name : CRUST.RD
Sample identification : crust from batch#34
Measurement date/time : 5-DEC-94 1:27
Diffractometer system : 1
Generator settings : 40 kV, 30 mA
Cu alpha1,2 wavelengths : 1.54060, 1.54439 Ang
Step size, sample time : 0.015 deg, 1.00 s, 0.015 deg/s
Monochromator used : Yes
Divergence slit : Automatic (Irradiated sample length: 10.0 mm)

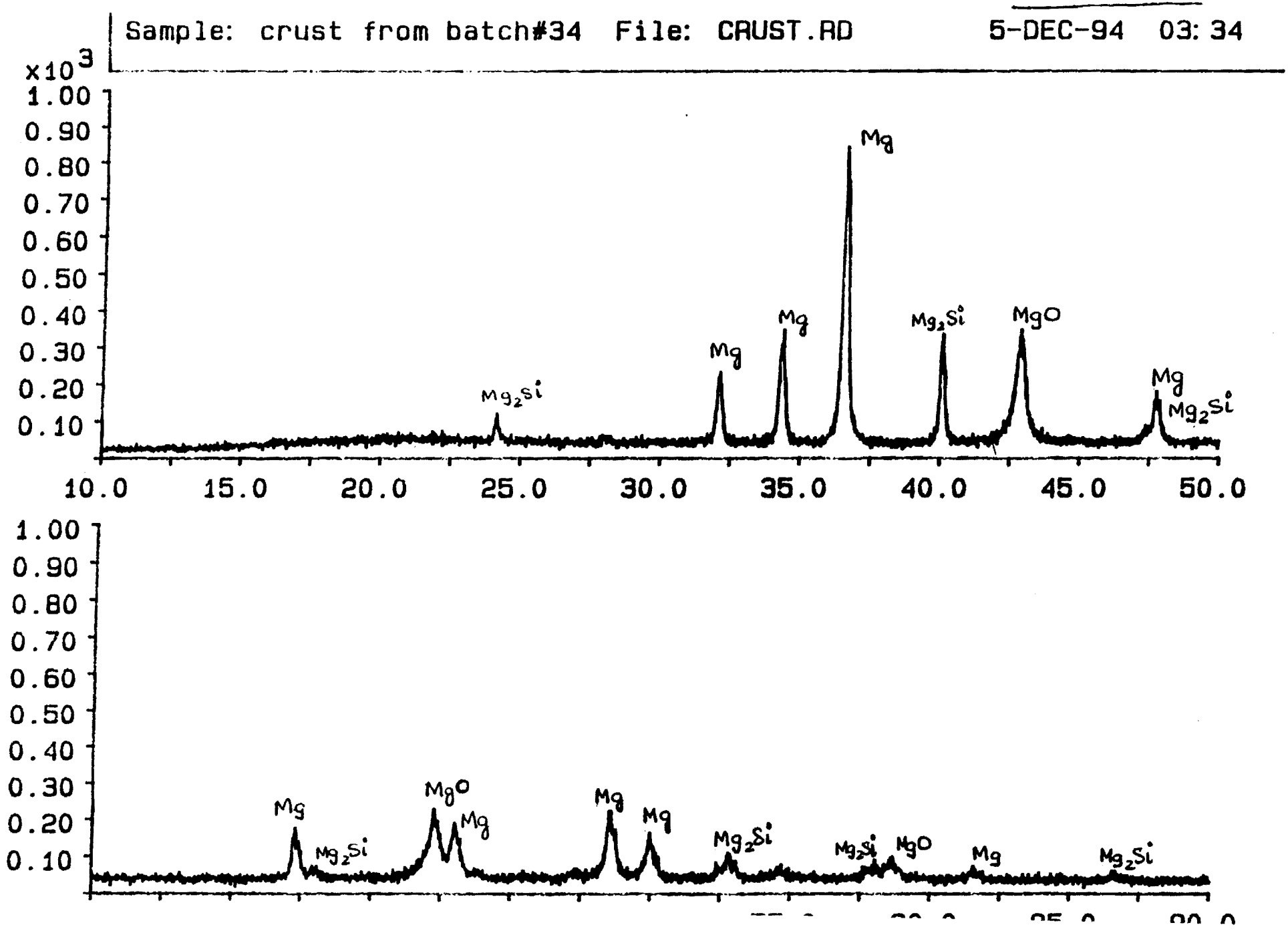
Analysis program number : 3
Peak angle range : 10.000 - 90.010 deg
Range in D spacing : 1.08927 - 8.8382 Ang
Peak position criterion : Top of smoothed data
Cryst peak width range : 0.00 - 2.00 deg
Minim peak significance : 1.00
Number of peaks in file : 20 (Alpha1: 19, Amorphous: 0)
Maximum intensity : 745. cts, 745.3 cps

Peak	Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D spac (Ang)	I/Imax (%)	Type A1	Type A2	Type Ot	Sign
1	24.1375	0.15	61.	38.	3.6841	8.16	X	X		1.70
2	28.0100	0.30	16.	38.	3.1830	2.15	X	X		1.07
3	32.1050	0.18	174.	38.	2.7857	23.38	X	X		5.01
4	34.3250	0.24	279.	40.	2.6105	37.42	X	X		13.18
5	36.5250	0.07	745.	38.	2.4581	100.00	X	X		1.95
6	40.0025	0.04	250.	34.	2.2521	33.50	X	X		1.29
7	42.8625	0.33	276.	41.	2.1082	36.97	X	X		13.80
8	47.7025	0.12	119.	38.	1.9050	15.94	X	X		1.10
9	57.2675	0.12	123.	34.	1.6074	16.53	X	X		1.23
10	58.0075	0.30	29.	35.	1.5887	3.91	X	X		1.45
11	62.2300	0.12	177.	37.	1.4906	23.73	X	X		1.29
12	62.9875	0.18	142.	37.	1.4745	19.00	X	X		2.45
13	67.3000	0.36	18.	37.	1.3901	2.37	X	X		1.07
14	68.5325	0.12	172.	36.	1.3681	23.03			Ot	1.48
15	69.9725	0.15	110.	36.	1.3434	14.79	X	X		1.66
16	72.8075	0.24	58.	35.	1.2980	7.75	X	X		1.48
17	74.6700	0.72	18.	35.	1.2701	2.37	X	X		3.24
18	78.6175	0.18	53.	34.	1.2159	7.15	X	X		1.12
19	81.6025	0.36	21.	32.	1.1788	2.84	X	X		1.45
20	86.6625	0.72	11.	30.	1.1225	1.46	X	X		2.24

Hard crust.


Sample: crust from batch#34 File: CRUST.RD 5-DEC-94 03:53
x10 3
1.00
0.80
0.60
0.40
0.20
△ – MgO
○ – Mg
× – Mg2Si
10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0
100.0
80.0
60.0
40.0
20.0
PERICLASE, SYN
4- 829
(MgO)
Mg
4- 770
Mg2Si
35- 773

Hard crust


Sample: crust from batch#34 File: CRUST.RD 5-DEC-94 03:34
x10^3
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
Mg
Mg
Mg
Mg
Mg2Si
Mg2Si
Mg2Si
MgO
Mg
Mg2Si
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
Mg
Mg2Si
MgO
Mg
Mg
Mg
Mg2Si
Mg2Si
MgO
Mg
Mg2Si

MICROTRAC DATA: MANUAL MODE
measurem't/present set: [illegible]
7997 0.12-39.0 SPA res: ORMAL
chan select bounds: 0.12- 39.00
progression: standard = chans:17
sample date/time: 12/03/91 [illegible]
sample ident: TA BALL MILL[illegible]
sample [illegible]
set code:
account =:VENKY printer: ON
run time: 30 sec. run =: 100/ 3
sample preparation code:
notes: Powder dispersed in water
with a drop of DARVAN #7 as
dispersing agent. sonic 5 min.

Esc-exit F2-commands

[illegible]	[illegible]	[illegible]
[illegible]	100.	[illegible]
2.11	99.[illegible]	[illegible]
1.50	96.8	1.1
1.12	97.1	1.1
0.82	98.[illegible]	1.7
0.60	92.[illegible]	5.4
0.43	86.[illegible]	5.7
0.28	80.1	5.9
[illegible]	[illegible]	[illegible]
[illegible]	71.[illegible]	[illegible]
0.09	65.8	5.6
0.01	9.1	5.6
0.06	3.5	2.6
0.43	2.5	1.1
0.34	1.4	0.4
0.24	0.9	0.4
0.17	0.5	0.5

summary data
cv: [illegible]
%10: 1.10
%50: 2.70
%90: 14.37
mv: 16.70
cs: 2.008
mi: [illegible]
[illegible]: [illegible]
ma: 2.33

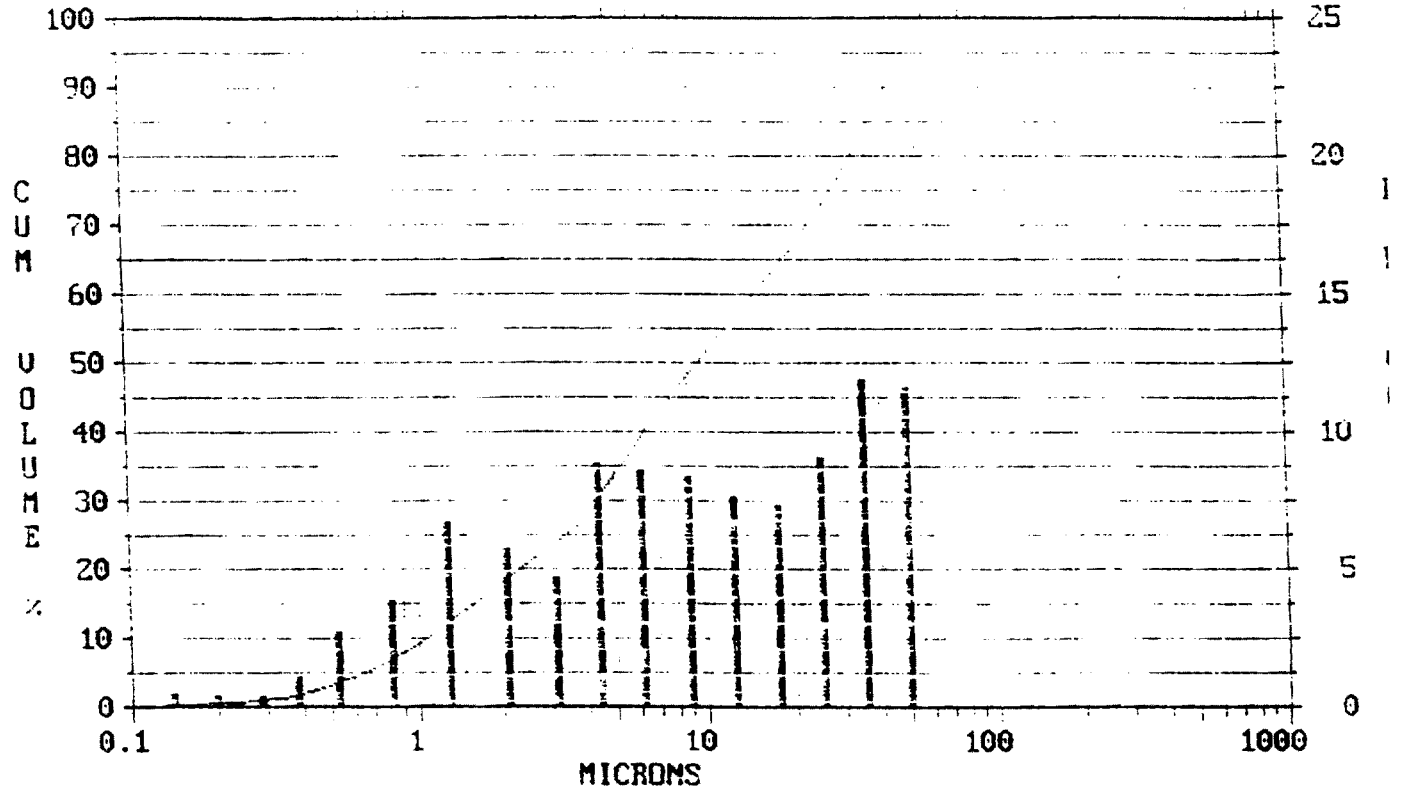
parameters	
name	value
smpl amt	
disprsnt	
disp amt	
disp med	
dmed amt	
agitat'n	
agit tim	
circul'n	
circ tim	
param =1	
param =2	
param =3	

Dr. Logan,

I haven't made copies of the data. There's a problem with the laser alignment which I could not fix. I'll talk to Dr. Cochran today and correct the problem. Full particle size data should be available next monday.

Venky

TA BALL MILLED 4 HR
TA 6hr #1
Record Number: 773



GRAPHITES FOR HOT PRESSING

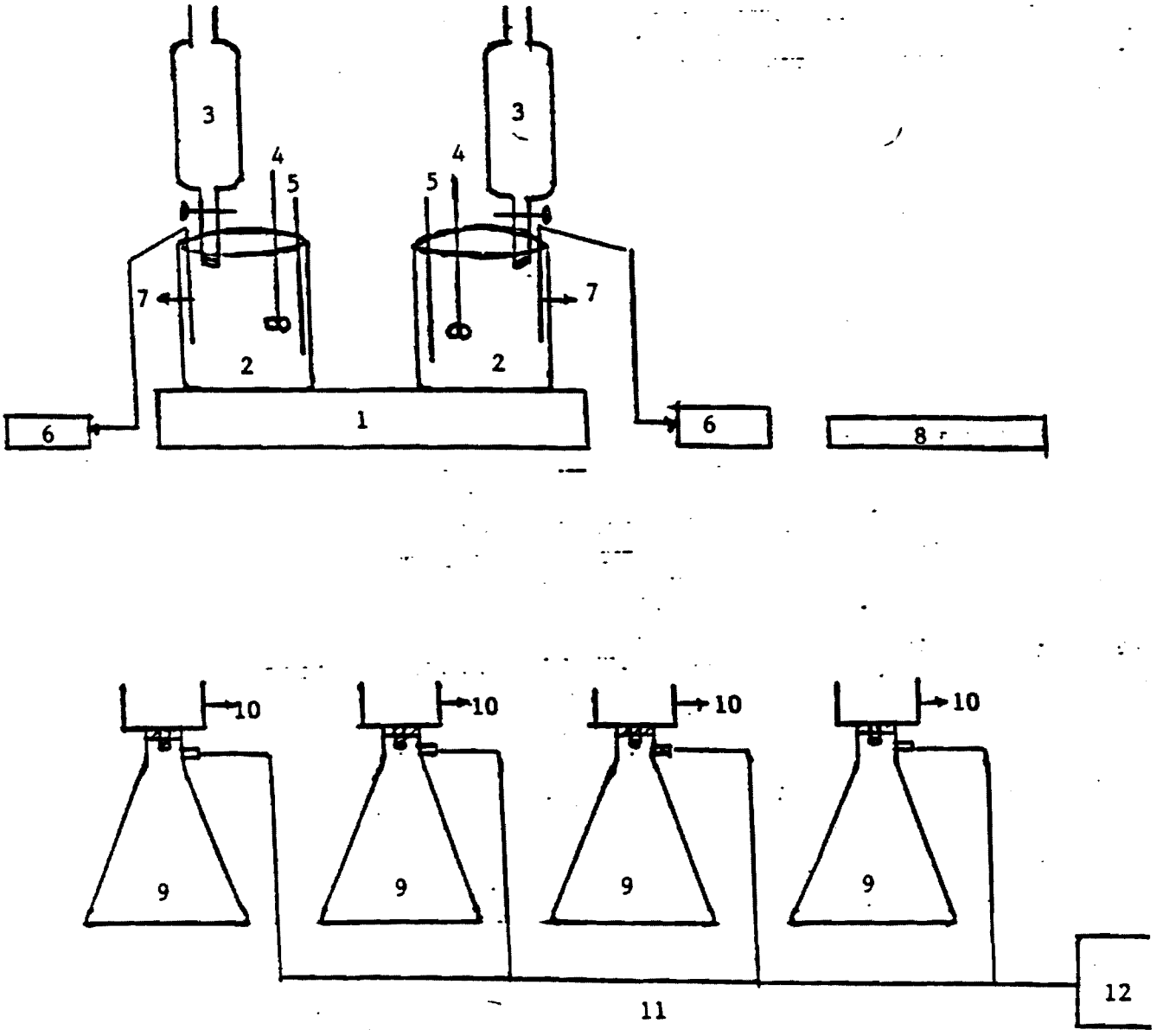
	UNOCAL (POCO)			SGL Carbon
	PGCS-3	XT	TM	R7340
Mechanical Properties				
Compressive strength (psi)	9,000	12,500	16,000	13,000
Flexural strength (psi)	5,000	6,500	9,000	6,500
E (psi x 10^6)	1.5	-	-	-
Hardness (Shore scleroscope)	45	-	65	-
CTE (micro in/in °F)	1.9	4.2	4.5	16

Notes:

1 PGCS-3, PGCS-1 have been discontinued by POCO

2 XT and TM grades are available in 3"od, 6"od, and 4"od.

3 R7340 grade from SGL is available in 3"od, 6"od, 4"od, and 8"od.



Schematic showing leaching process

1	Hot plate
2	Beakers (4000ml)
3	Separatory funnels (500-1000ml)
4	Stirrer motors with teflon stirrers
5	Thermometers
6	PH meters
7	PH probes
8	Strip chart recorder
13	Ring stands (not shown)
8	Strip chart recorder
9	Flasks/Fleakers (1000ml)
10	Plastic funnels and filters
11	Tygon tubing
12	Vacuum pump
14	Clamps (not shown)

COMPOSITE POWDER INVENTORY
12/12/94

POWDER

	MASS-G	MASS-LB
UNMILLE	8544.70	18.82
MILLED	7311.20	16.10
TOTAL	15855.90	34.92

GIVEN TO AEM

UNMILLE		10507.8	23.14
MILLED	HR 8	80	0.18
	HR 15	85	0.19
	HR 30	75	0.17
	SAMP-12	180	0.40
	TOTAL	10927.8	24.07

RETURNED

MILLED			
MIN 10	955.5	2.10	
MIN 20	976.6	2.15	
MIN 45	903.9	1.99	
HR 2	931.5	2.05	
MIN 45	968.0	2.13	*
MIN 45	1052.8	2.32	*MASS WITH BAG*
MIN 45	966.5	2.13	*
TOTAL	6754.8	14.88	

*** THE REMAINING UNMILLED POWDER WAS RECEIVED FRIDAY***

TOTALS

PRODUC	28694.7	63.20	THIS DOES NOT INCLUDE BATCHES 2-9

PURE POWDER INVENTORY
DEC. 12, 1994

TOTAL

MASS- G		MASS -LB	
GROSS	NET	GROSS	NET
20220.95	22139.3	44.54	48.76

AVG -G		AVG -LB	
GROSS	NET	GROSS	NET
505.52	491.98	1.11	1.08

AVG %	
GROSS	NET
84.25	82.00

PURE BALL MILLING

	MASS-GROSS	MASS NET	% YIELD
6	525	520.8	99.20
7	510.4	509.6	99.84
8	449.3	438.5	97.60
9	506.3	495.2	97.81
10	368	366.7	99.65
11	317	314.8	99.31
12	248	232.9	93.91
13	329	323.3	98.27
14	300	288.5	96.17
15	540.9	538.2	99.50
16	520.2	517.7	99.52
17	537.8	537.7	99.98
18	526.6	522.8	99.28
19	495	495	100.00
20	509.3	502.4	98.65
21	501.7		0.00
22	517.2		0.00
23	532.8		0.00
24	538.7		0.00
25	535		0.00
26	527.5		0.00
27	537.2		0.00
28	514.5		
29	465		
30	487		
31	492.6		
32	478.8		

AVG-MASS	AVG-MASS	AVG-YIEL
474.47	440.27	98.58

AEM Project A-9859
12/12-12/16

A. The leaching has begun with two batches of powder being leached. Both batches have gone through two washings and will go through a sulfur wash as a result of the XRD.

B. The hot press base has been renovated by Charles, Gautam and Guillermo. The base was found to be warped so the refractory brick and two silicon carbide bricks had to be replaced along with the kaowool paper between them. New Kaowool board was cut for the base insulation. More alumina bubble was purchased and added to the insulation. The thermocouple in the water bath has been replaced along with the gauge.

C. The 6th hot press run finished without a problem. The results were a disk with a density of only 3.79 g/cm3. The soak time was 2 hours and 10 minutes. A new grade of graphite, XT, was used in the die and the punches. This die has a larger expansion coefficient. This allows for a wider disk but when the die cools it is difficult to extract the disk without damage to the die.

D. There have been two 5 pound samples received from Tioxide Americas. These are samples of TiO2/B2O3 mixture. Sample one was mixed for 30 seconds and the second sample was mixed for 90 seconds.

E. Venkatesh conducted an experiment that measured the temperatures for the composite reaction. This was done in a small crucible with two thermocouples embedded in the walls. The response time of the thermocouple was slow because of the thickness of the crucible. In the next experiment the thermocouples will be placed inside the crucible.

HOT PRESS

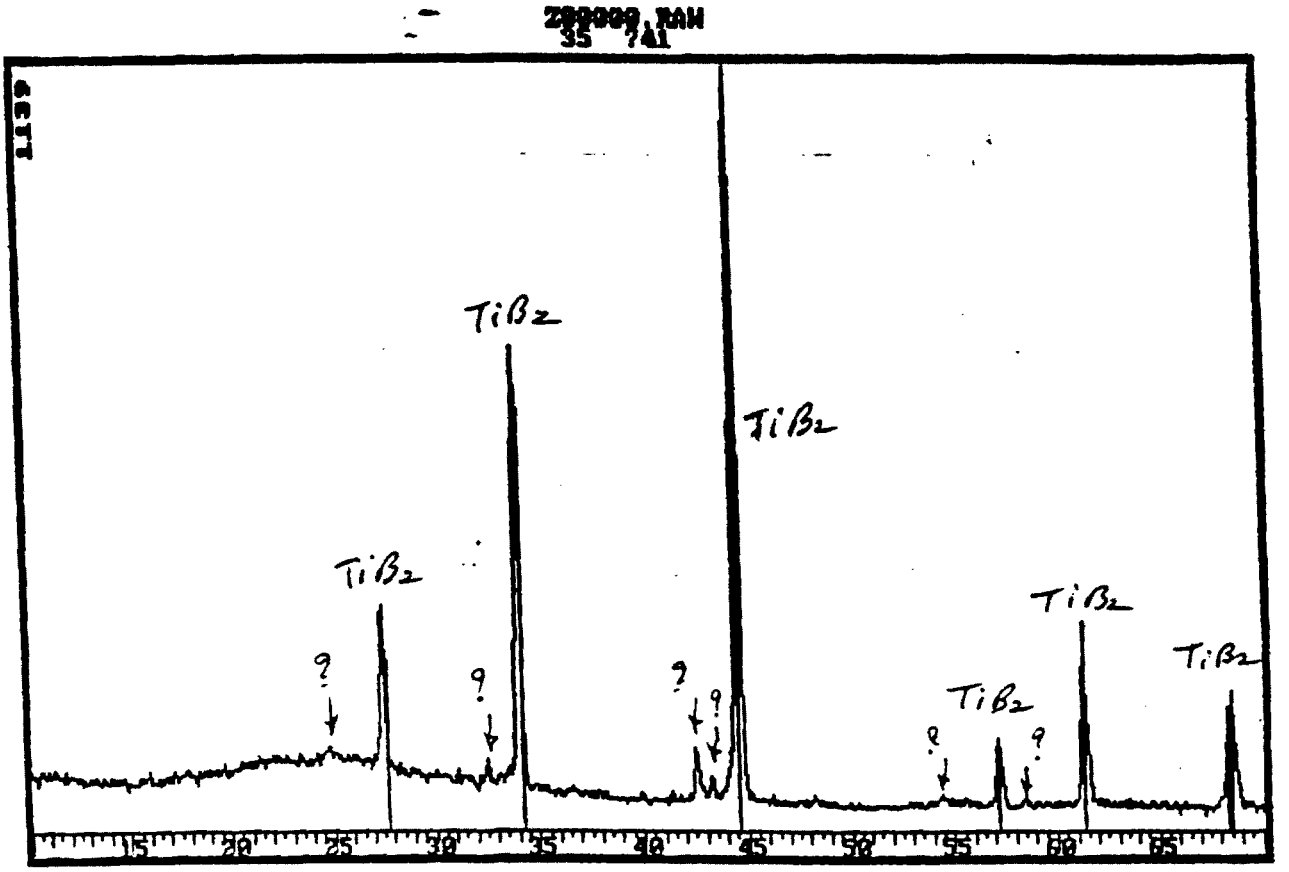
PARAMETERS

RUN	TYPE POWDER	MASS {G}	DRY-PRESS {PSI}	FINAL-PRESS {PSI}	FINAL TEMP {C}	RAMP TIME {MIN}	SOAK TIME {HOURS}	THERMOCOUPLE TYPE
1	T/A COMP	240.0	3374	5399	1500	25	1:51	B
2	T/A COMP	239.7	3374	6298	1500	20	2:55	S
3	T/A COMP	239.8	3374	6501	1525	25	1:54	S
4	T/A COMP	239.9	3374	6501	1580	35	1:35	S
5	T/A COMP	239.8	3374	6501	1580	24	NA	S
6	T/A COMP	239.8	3374	6501	1580	20	2:10	S

DISK DATA

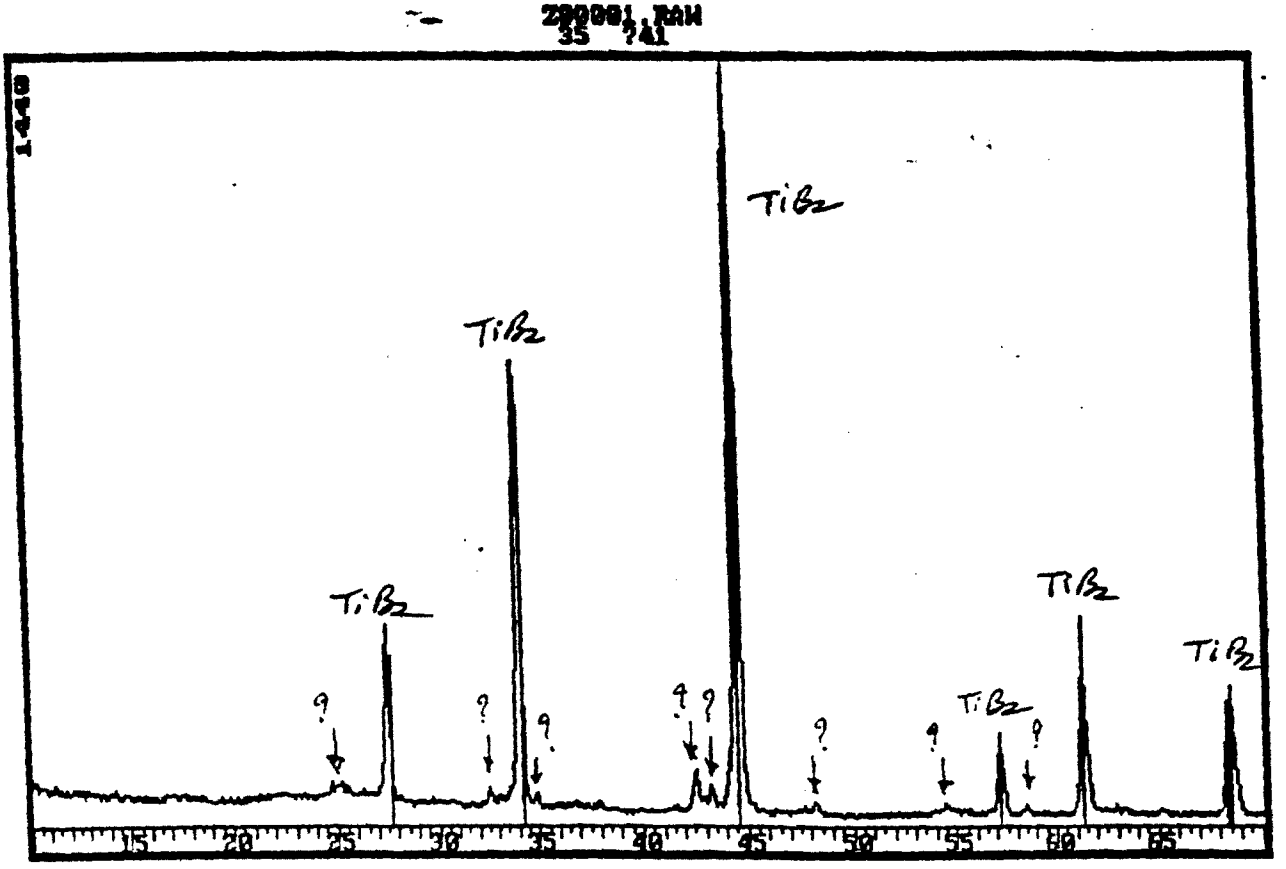
DISK	DIMENSIONS DIAMETER {IN}	DIMENSIONS THICKNESS {AVG-IN}	GROSS MASS {G}	NET MASS {G}	THEORETICAL DENSITY {G/CM3}	TRUE DENSITY {G/CM3}	PERCENT DENSE
1	3	0.545	240.0	238.50	4.14	3.79	91.55
2	3.0465	0.55	239.7	238.13	4.14	3.72	89.86
3	3.039	0.512	239.8	233.79	4.14	3.93	94.93
4	3.041	0.495	239.9	233.50	4.14	4.04	97.58
5	3.048	0.612	239.8		4.14		
6	3.053	0.543	239.8	236.51	4.14	3.80	91.79

Leach 2, 2 wash



TiB2

Leach 1, 2 wash



TiB2

AEM WEEKLY PROGRESS REPORT
12/19/94-12/23/94

1. T/A Hot Press Run

Hot press run #7 was done on Tuesday (12/20/94). The disk turned out to be 95.65% dense after polishing. The ramp time was 25 min and the soak time was 2 hours 50 minutes. The temperature was 1580 C and the pressure was 2890 line pressure. It is really hard to remove the disk from the new XT graphite because of the high coefficient of thermal expansion.

Graphite For Hot Pressing

	UNOCAL (POCO)			SGL Carbon
	PGCS-3	XT	TM	R7340
Properties				
Compressive strength(psi)	9,000	12,500	16,000	13,000
Flexural strength(psi)	5,000	6,500	9,000	6,500
E (psi x 10^6)	1.5	-	-	-
Hardness	45	-	-	-
CTE (micro in/°F)	1.9	4.2	4.5	16
Electrical Resistivity (u.ohm.in)	600	500	500	470

2. TiB2 SHS Experiments

2a: Vacuum Chamber (experimental setup & reactions):

The argon vacuum chamber was finished on Tuesday and is working nicely. The chamber is flushed out by alternately vacuuming the chamber and pumping in argon. When a reaction is to be set off, there is a constant stream of argon flowing through the chamber. The procedure is documented in Notebook #2. There have been 5 reactions set off in the chamber successfully. These are as follows:

	Mg	TiO2	B2O3	Total
stoichiometric:	11.21	7.37	6.42	25.00g
20% excess B2O3:	11.21	7.37	7.71	26.29g
40% excess B2O3:	11.21	7.37	8.99	27.57g
20% excess Mg:	13.45	7.37	6.42	27.24g
40% B2O3/20% Mg:	13.45	7.37	8.99	29.81g

2b: **XRD Results:**

a: The stoichiometric composition - Peaks are TiB2, MgO, Mg-borates, and Mg-titanates.

b: As the amount of B_2O_3 is increased (from 20% excess to 40% excess), the peak heights of Mg-titanate decreased and the peak heights of Mg-borate increased.

c: Addition of 20% excess Mg to a stoichiometric mixture containing 40% excess B_2O_3 still further reduces the peak heights of Mg-titanate.

d: Leached samples analyzed after the second wash do not show Mg-titanate peaks. The samples contain mainly TiB2, with slight amounts of MgO, Mg-borate, and Mg-Ti-Oxide-Borate.

3. Miscellaneous

1-Received one five pound sample of Tioxide A-hr CS-21766 from Tioxide.
2-Received one container of 36 kg of Mg dust from Reade manufacturing.
3-Received processed TiB2/MgO Deagglomerate from Union Process.
4-A 2 pound sample of mixed TiO_2/B_2O_3 was sent for Paul to Fike Testing Services.

T/A HOT PRESS

PARAMETERS

RUN	TYPE POWDER	MASS (g)	DRY-PRESS (PSI)	FINAL-PRESS (PSI)	FINAL TEMP (C)	RAMP TIME (MIN)	SOAK TIME (HOURS)	THERMOCOUPLE TYPE
1	T/A COMP	240.0	3374	5399	1500	25	1:51	B
2	T/A COMP	239.7	3374	6298	1500	20	2:55	S
3	T/A COMP	239.8	3374	6501	1525	25	1:54	S
4	T/A COMP	239.9	3374	6501	1580	35	1:35	S
5	T/A COMP	239.8	3374	6501	1580	24	NA	S
6	T/A COMP	239.8	3374	6501	1580	20	2:10	S
7	T/A COMP	239.8	3374	6501	1580	25	2:50	S

NOTE:
Run 1 to 5 - POCO PGCS-3 Dies
Run 6 & 7 - POCO XT Dies

DISK DATA

DISK	DIMENSIONS DIAMETER (IN)	DIMENSIONS THICKNESS (IN)	GROSS MASS (g)	NET MASS (g)	THEORETICAL DENSITY (G/CM3)	TRUE DENSITY (G/CM3)	PERCENT DENSE
1	3	0.545	240.0	238.50	4.14	3.79	91.55
2	3.0465	0.55	239.7	238.13	4.14	3.72	89.86
3	3.039	0.512	239.8	233.79	4.14	3.93	94.93
4	3.041	0.495	239.9	233.50	4.14	4.04	97.58
5	3.048	0.612	239.8		4.14		
6	3.053	0.543	239.8	236.51	4.14	3.80	91.79
7	3.041	0.473	239.8	222.46	4.14	3.96	95.65

AEM WEEKLY PROGRESS REPORT

1/3/95-1/13/95

1 T/A Hot Press Run

Hot press run #8 was conducted on Thursday (1-5-95). The powder was initially dry pressed to 2500 psi line pressure. The ramp time was 22 minutes and the soak time was 3 hours and 10 minutes. The final soak temperature and final line pressure were kept at 1580 C and 2890 psi respectively.

The purpose of this run was to generate a CTP curve. However, during the ramp up period the linear dial gage to measure the travel was found to show the upward movement. During the soaking period, the gage was showing the downward movement but was not consistent. In order to know whether or not the gage rod was sticking, the bar which supports the gage rod was moved manually several times during the run. The gage would move downward for a while and then stop. It seemed that the gage was sticking. We were unable to obtain the true measurements (i.e. decrease in travel of the gage with respect to temp and pressure).

It was decided to complete the run. The disk was found to be 94.9% dense after polishing. There was some powder deposited on the surface of the top plunger but was not of a significant amount as compared to the previous run. This was consistent with the negligible weight loss after hot pressing.

This run was conducted with POCO XT graphite die and plungers. During the next run, we will use the old POCO PGCS-3 graphite die and plungers, and a new dial gage. CTP curve will be obtained.

2 Density Measurement

The method to measure the density of the hot pressed disk has been modified to obtain a precise measurement of density. Removal of the graphoil is done by heating the disk at low temperature and using a scraper. Polishing using a diamond wheel is done for a long period to completely remove the surface porosity and residual graphoil. The disk is dried in an oven at low temperature for a long period (1 to 3 hrs). The disk is immersed in water for a long period (1 to 2 hrs) prior to taking the reading.

After repolishing the rechecked density for disk 4 and 7 was 98.05% and 96.37% respectively. The weight loss for samples 4 and 7 after repolishing was not significant. Samples will show some weight loss and reduction in thickness if polished for a long period. However, a more precise measurement of density can be obtained with the modified procedure than the previous method.

Disk	Wt.		Density in percent	
	1 polish	2 polish	1 polish	2 polish
4	233.50	233.08	97.58	98.05
7	222.46	221.98	95.65	96.40
8		224.7		94.90

3 **TiB_2 Experiments:**

3a: TiB2 Leaching

We devoted the entire last week for leaching of TiB_2. There have been six batches leached, sulfur washed and dried. We have between 380 to 465 gm of leached powder to hot press (~400gm per week). There is a need to improve the filtration mechanism to expedite the process, perhaps a large vacuum pump, large capacity filter flasks and funnels. The leaching process can also be improved to increase the production perhaps by using large beakers, and bigger hot plates and stirrers.

3b: XRD of Powders:

The data of leached samples and vacuum experiments are being evaluated by Shin this week.

4 **Miscellaneous**

1-Received two pounds of anatase TiO2 (Unitane 0-110) from Kemira
2-Received one bag of Tioxide A-HR, CS-21766 from Tioxide Canada Inc (Henschel).
3-Received one pound of anatas TiO2 pigment dry from Henschel.
4-Received Lindberg furnace from Oxley Research, Inc.

5 Scheduled Work (this week)

Leaching of TiB_2
Hot pressing of TiB_2 and T/A (obtain one disk each)
Obtain CTP curves for TiB_2 and T/A
Evaluate XRD results.

Electrodes
3, HP inserts

AEM WEEKLY PROGRESS REPORT 1/16/95-1/20/95

1) Evaluation of XRD data of as reacted and leached sample
2) Steel bucket experiment and XRD evaluation
3) Leach #8 - modified process
4) Hot press
5) TiB_2 and TiB_2-Al_2O_3 composite inventory update
6) Future works:
   a) Should receive dial gage today.
   b) Hot pressing of blank die for thermal expansion measurement.
   c) Hot pressing of pure TiB_2
   d) Continue leaching
   e) Quantitative analysis of XRD data.

Weekly Report 1/17 - 1/20/95

1. XRD Ananlysis of As Reacted Sample

Table I. Effect of batch composition and reaction atmosphere on the primary XRD intensities of each reaction preoduct (unit: count per sec).

	TiB_2	MgO	TiB_2/MgO	Mg_2TiO_4	$Mg_3B_2O_6$
Air(50M+39B)	961	2836	0.339	46.9	176
Air(stoi)	925	2125	0.435	270	180
Ar(stoi)	891	1891	0.471	266	188
Ar(20B)	1023	1844	0.555	203	250
Ar(40B)	1015	1666	0.609	195	364
Ar(20Mg)	977	2364	0.413	176	137
Ar(40B+20M)	1017	2067	0.492	130	309

From the viewpoint of maximum TiB_2 peak intensity, 20% excess B_2O_3 composition is suggested for powder production.

2. XRD Analysis of 50M+39B Sample after Leaching

Table II. XRD analysis of 50M+39B sample after leaching. This sample was prepared in air (600g batch).

	TiB_2	MgO	MgBTiO	Mg_2TiO_4	$Mg_3B_2O_6$	TiO_2
Before Leaching	961	2836	superimposed to MgO	46.9	176	Not observed
Leach #1	1575	90	111			85
Leach #2	1906	76	105			78
Leach #3	1797	82	134			103
Leach #5	1563	87	116			125
Leach #6 abnormal	1189	75	75			211
Leach #7	1531	100	114			126
Leach #8 modified	1561	82	111			135

After leaching, MgO, MgTiBO, and TiO_2 were noticeable second

phases. TiO_2 is interpreted to have formed during leaching. During the leach #6, pH of the soulution suffered abnormalously low pH (lower than pH of 1) for about 3 min due to accident. This resulted in an enhanced TiO_2 peak intensity with diminished MgO and MgTiBO peak intensities. Obviously, lower pH is helpful for the elimination of Mg-oxides. However, for the elimination of TiO_2, pH control of higher than 2.0-2.5 is suggested.

Pure TiB_2 has been reported that its densification reached only ~ 75% at 1900°C by hot pressing. However, residual oxides are interpreted to enhance densification of TiB_2 via liquid phase sintering so that lower temperature densification with increased product density is obtained. However, this will sacrifice high temperature strength of the densified TiB_2.

During the week of 1/23-1/27, quantitative analysis of TiB_2, MgO, and TiO_2 will be performed by Shin using the external standard method (unless otherwise asked to do other more important things).

3. Bucket Reaction Analysis

Al_2O_3/TiB_2 composite was reacted in a steel bucket in air.

	TiB_2	Al_2O_3	$Al_5(BO_3)O_6$
Top cake	703	683	273
Bottom cake	1073	1018	123

AEM WEEKLY PROGRESS REPORT

1/16/95-1/20/95

TiB_2 INVENTORY

	Grams	Pounds
Unmilled		
Discarded	269.9	0.60
Milled (30 min)	12383.10	27.30
Leached	3440.00	7.60
Total	15628.10	34.40

T/A INVENTORY

	Grams	Pounds
Unmilled (on hand)	19416.90	42.80
Milled (Ga Tech)	4547.10	10.00
Milled (Union Process)	67548.00	14.90 — UP/30 m
Total	30718.80	67.70

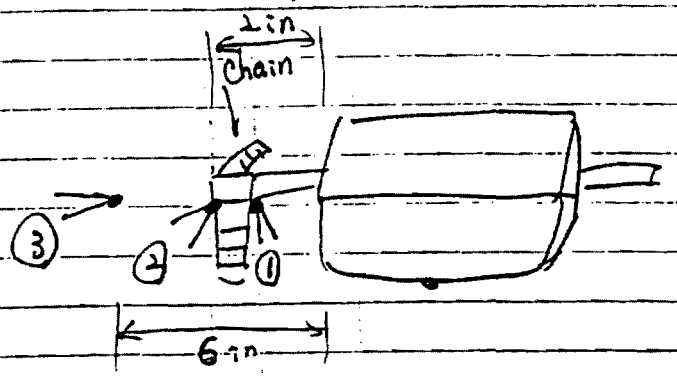
1 Submitted to AEM 80+85+75+180 = 420gm (0.9 lb) (John Winters)

2 Steve Beers picked up Union Process ------- milled powder (4 plastic bottles, 1/19/95) 4844.2 gm (10.7 lb)

1-17-95

2:00 p.m.

Composites TA 400g Batch in Air



Thermocouple ① : 18°C → 78°C } red line 50mV Scale 30 Cm/min

② : 18°C → 20°C } blue line

③ : 18°C → 20°C black pen — 20/0 mV 30 Cm/min

{ Charles Guillermo Shin Gautam
Paul Joel }

Procedure : see 1 N.B. 1
Materials : see p2 NB 1
LOT #'s TiO_2 - 942932
B_2O_3 - 934952A
Al - see p 2

- Hot Wire ignition
- 400g batch
- Very violent green/white

Continued on Page

Read and Understood By

Signed _____ Date _____ Signed _____ Date _____

Interim report

Evaluation of XRD Results from Thermite Reactions in $TiO_2-B_2O_3-Mg$ System

Data Obtained by Advanced Ceramics and Composites Group

Reported by Hyunho Shin

January 20, 1995

1. INTRODUCTION

In order to optimize the formation of TiB_2 by a thermite reaction ($TiO_2 + B_2O_3 + 5Mg = TiB_2 + 5MgO$), various compositions of batches were prepared and reacted. (Benefits of thermite reaction will be discussed here as compared to other preparation methods)

2. EXPERIMENTAL PROCEDURE

2-1. Reaction

Two series of batches were with excess Mg and with excess B_2O_3. Most of the reactions were performed in air and vacuum[1] atmosphere except 50% excess Mg plus 39% excess B_2O_3 composition.

2-2. Characterization

Reaction products were pulverized using mortar and pestle. X-ray diffraction (XRD)[2] was performed using Cu K-alpha radiation with step size of 0.02° and duration time of 1 sec at each step.

3. DATA AND RESULTS

3-1. Effect of Reaction Atmosphere

Table I. Effect of reaction atmosphere on primary XRD peak intensities of reaction products (unit: counts per sec)

	TiB_2	MgO	TiB_2/MgO	Titanates	Borates
Air(50M39B)	960.9	2835.9	0.339	46.9	175.8
Air(stoi)	925.0	2125.0	0.435	270.0	180.0
Ar (stoi)	890.6	1890.6	0.471	265.6	187.5

In air, Mg is consumed not only for the reduction of TiO_2 and B_2O_3 but also for the formation of MgO by reacting with atmospheric oxygen. This results in an increased MgO peak intensity of air-reacted sample (decreased TiB_2/MgO ratio) as compared to vacuum-reacted sample. However, less available Mg in air-reacted sample resulted in enhanced TiB_2 formation. The heat of formation of MgO is interpreted to have fostered the reduction of TiO_2 and B_2O_3 by remained Mg.

The formation of titanates and borates are the results of

---

[1]Vacuum level was

[2]Rigaku Denki Co. Ltd., Model , Tokyo, Japan.

reaction between MgO and oxides (TiO_2 and B_2O_3).

$$2MgO + TiO_2 = Mg_2TiO_4 \text{ (titanate)}$$
$$3MgO + B_2O_3 = Mg_3B_2O_6 \text{ (borate)}$$

At a finite reaction rate, before all available Mg reduces oxides, previously oxidized Mg portion (MgO) consumes B_2O_3 and TiO_2 so that less chance of Mg/B_2O_3 and Mg/TiO_2 reactions results. Hence the formation of titanates and borates always results in a diminished TiB_2 formation.

In air-reacted sample, as temperature increases by the heat of formation of MgO, reaction of $Mg-TiO_2$ and $Mg-Al_2O_3$ are interpreted to be more favorable than $MgO-TiB_2$ and $MgO-B_2O_3$, so that formation of titanates and borates are diminished while TiB_2 formation is fostered, as observed in Table I.

3-2. Effect of Excess Mg Addition

Table II. Effect of excess Mg on primary XRD peak intensities of reaction products in vacuum (unit: counts per sec).

	TiB_2	MgO	TiB_2/MgO	Titanates	Borates
Stoichio.	890.6	1890.6	0.471	265.6	187.5
20 Mg	976.6	2363.6	0.413	175.8	136.7
$20Mg+40B_2O_3$	1017.1	2066.7	0.492	130.2	309.2

Addition of 20% excess Mg to stoichiometric batch would result in an increased interface area of Mg/TiO_2 and Mg/B_2O_3 (enhances TiB_2 formation) while reduce the chance of MgO/TiO_2 and MgO/B_2O_3 interfaces (diminishes titanates and borates formation). This is consistent with Table II.

As 40% excess B_2O_3 is added to the 20% excess Mg sample, Mg/B_2O_3 interface area is increased while Mg/TiO_2 area is decreased. The increased Mg/B_2O_3 area enhances the formation of borates (confirmed in the table) and boron source for TiB_2 formation. The decreased area of Mg/TiO_2 interface would result in a diminished titanates (confirmed in the table) and decreased amount of tanium source for TiB_2 formation. In other words, enhanced amount of boron source with diminished quantity of titanium source is expected. What was observed under this situation was enhanced TiB_2 formation. This implies that the provision of boron source has been the rate limiting factor in the TiB_2 formation.

3-3. Effect of Excess B_2O_3 Addition

Table III. Effect of excess B_2O_3 addition on primary XRD peak intensities of reaction products in vacuum (unit: counts per sec).

	TiB_2	MgO	TiB_2/MgO	Titanates	Borates
Stoic	890.6	1890.6	0.471	265.6	187.5
$20B_2O_3$	1023.4	1843.8	0.555	203.1	250
$40B_2O_3$	1015.2	1666.0	0.609	195.2	364.4
$40B_2O_3$+20Mg	1017.1	2066.7	0.492	130.2	309.2

Addition of 20 excess percent B_2O_3 results in an increased interface area of Mg/B_2O_3 (enhanced B_2O_3 reduction for boron source and increased borates formation) while it results in a decreased interface area of Mg/TiO_2 (diminished titanum source for TiB_2 formation and reduced titanates formation). Up to 20 excess percent B_2O_3, TiB_2 peak intensity increased. By the addition of 40 excess percent, available Ti source is interpreted to be too much limited while excess B_2O_3 fosters borates formation. This is responsible for the decrease in TiB_2 peak intensity at 40 excess percent batch.

The decrease in titanates formaton would foster the formation of 2 moles of MgO per mole of titanates, whille the increase in the borates formation would take up 3 moles of MgO per mole of borates. This would result in the decrease in MgO peak intensities.

The addition of 20% excess Mg to 40% excess B_2O_3 sample would increase Mg/B_2O_3 and Mg/TiO_2 interface area, lowering the chance of MgO/Al_2O_3 and MgO/TiO_2 contacts. This would be responsible for the diminished titanates and borates formation as compared to 40% excess B_2O_3 sample.

3-4. Effect of Leaching

After two times of nitric acid leaching followed by sulfur washing, MgO and titanates peak intensities were eliminated dramatically, while borate phase was hard to remove.

The leaching process was revised this week (1/13-1/20). Both powder and acid were poured into beaker simultaneously so that pH range was maintained below ~7. When powder was used up, pH was maintained 2~2.5. After this revised leaching, however, no appreciable difference was observed --- appreciable peak intensities of borates and TiO_2. We know that TiO_2 forms at low pH values during leaching. Based upon this result, controlling pH of 2~2.5 is not adequate to avoid TiO_2 formation. Higher range of pH values are suggested as controlling pH.

4. CONCLUSION

From the viewpoint of maximum yield of TiB_2, 20% excess B_2O_3 would be the best (highest TiB_2 peak intensity). However, The variation of TiB_2 peak intensity among different batches was not significant (890 - 1023). Considering leaching, borates was most

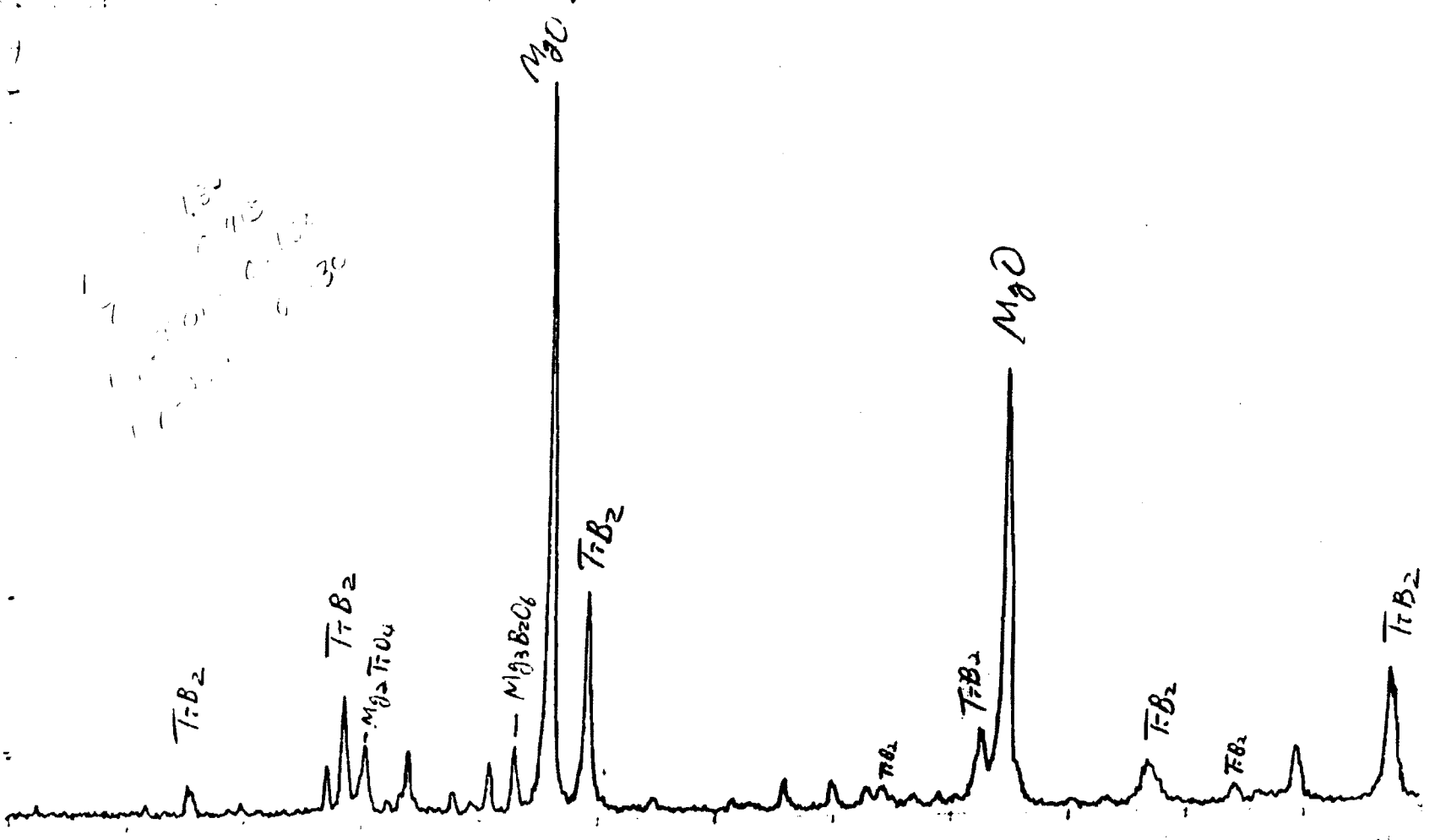
hard to leach out. Hence batches with excess B_2O_3 (always fosters excess borates) should be avoided --- 20% excess Mg composition (in vacuum) having least peak intensity of borates is suggested to be the best for TiB_2 synthesis at the present time. 20% excess Mg composition also has good TiB_2 peak intensity (977).

It is suggested to vary the composition of the mixed powder in air in order to determine the optimum composition for minimal borates with considerable TiB_2 formation.

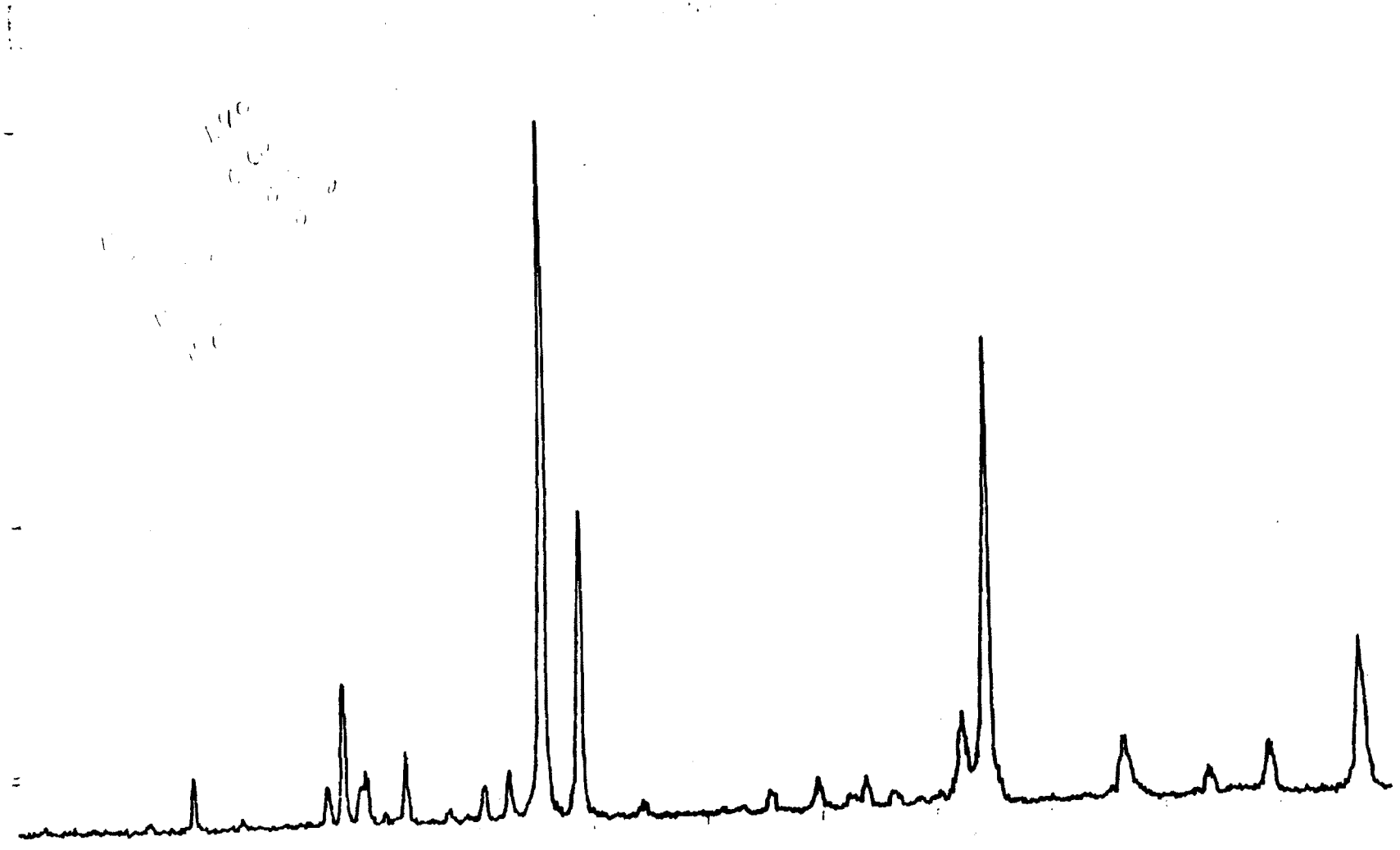
1M1B	—			1M20B				1M40B
5M1B	5M5B							
10M1B	10M5B	10M 10B						
20M1B								20M 40B

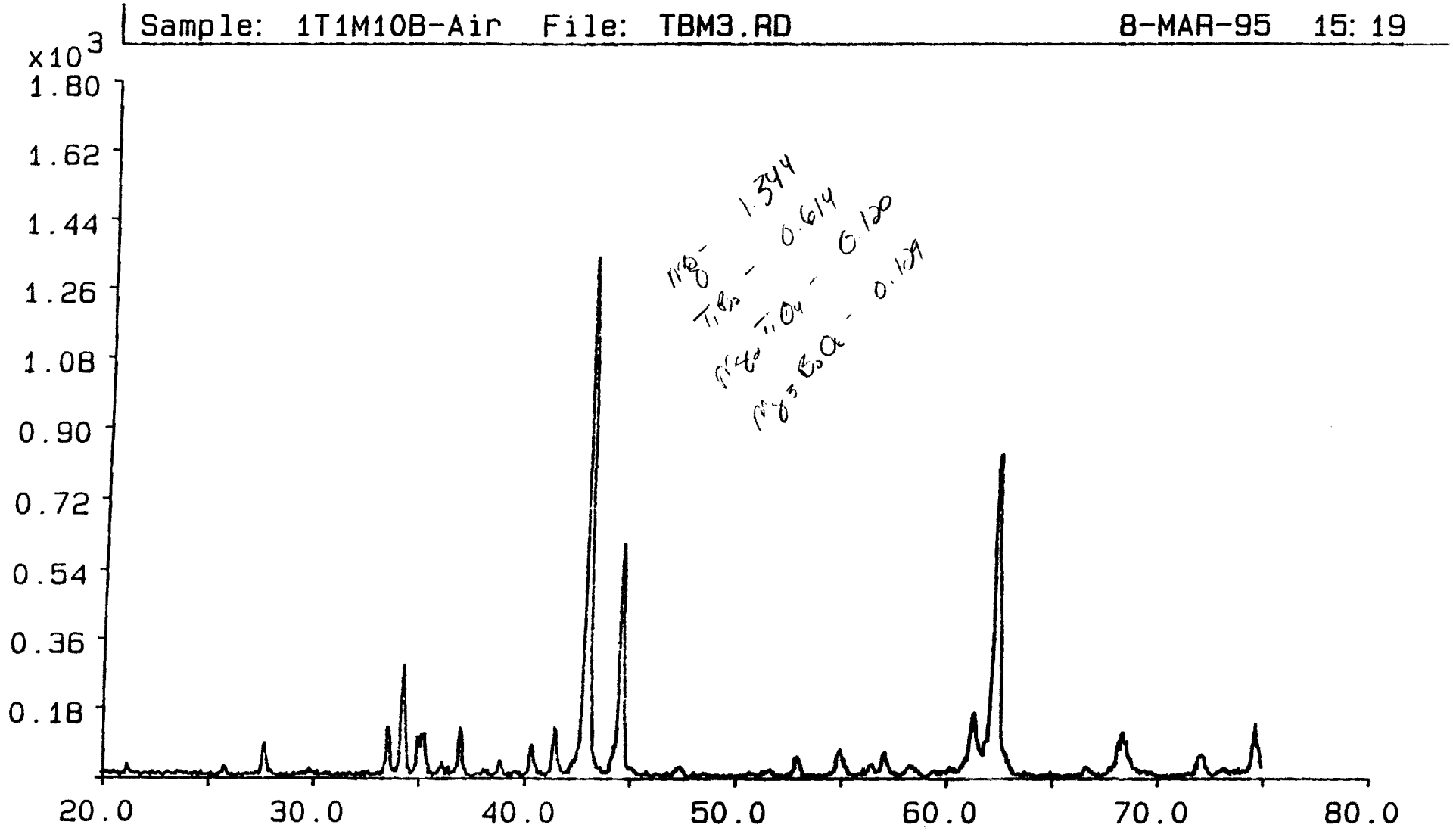
IM1B

IM1B-Air



TBA 2
Air 1M5B

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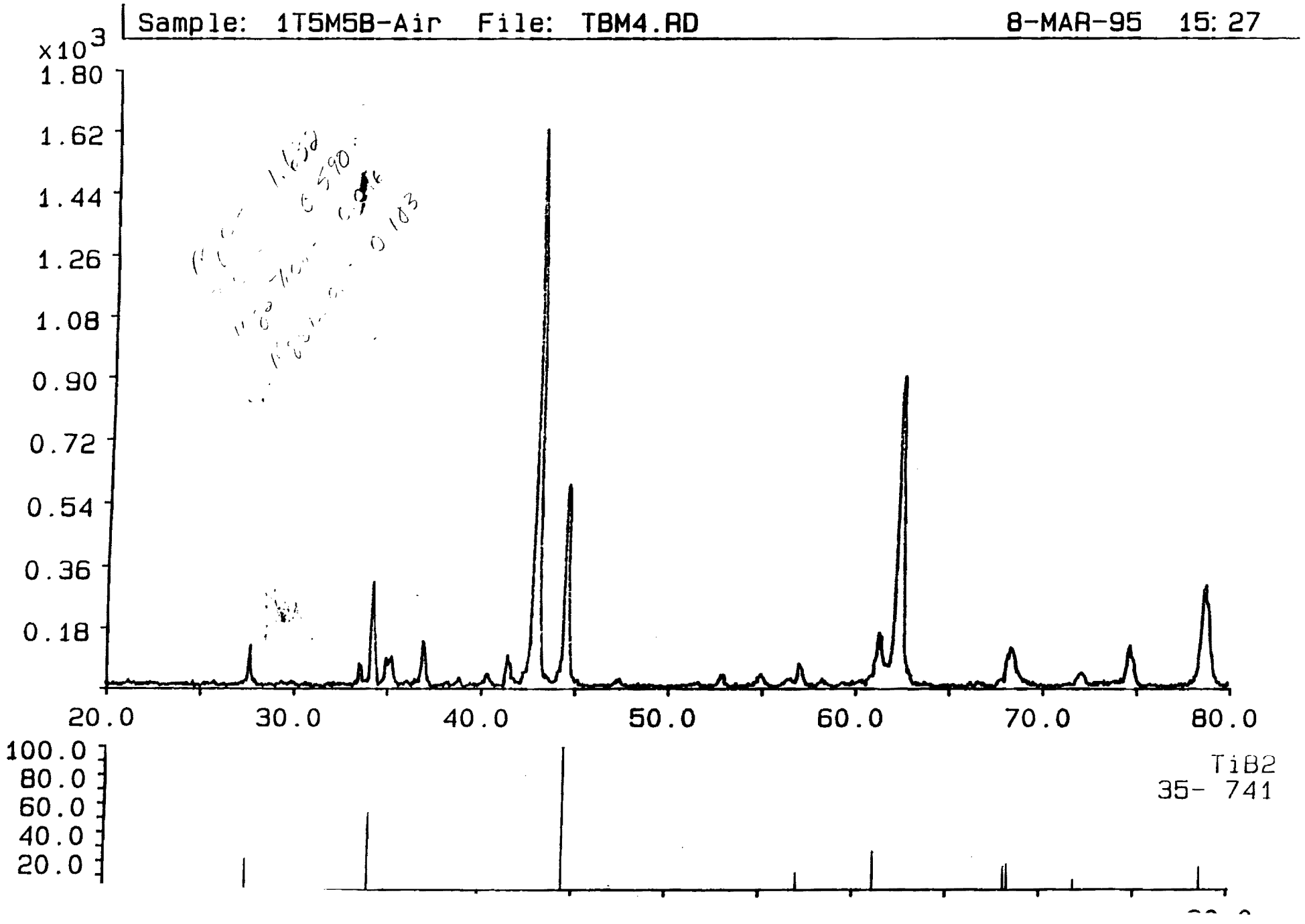
1.62
1.44
1.26
1.08
0.90
0.72
0.54
0.36
0.18
20.0
30.0
40.0
50.0
60.0
70.0
80.0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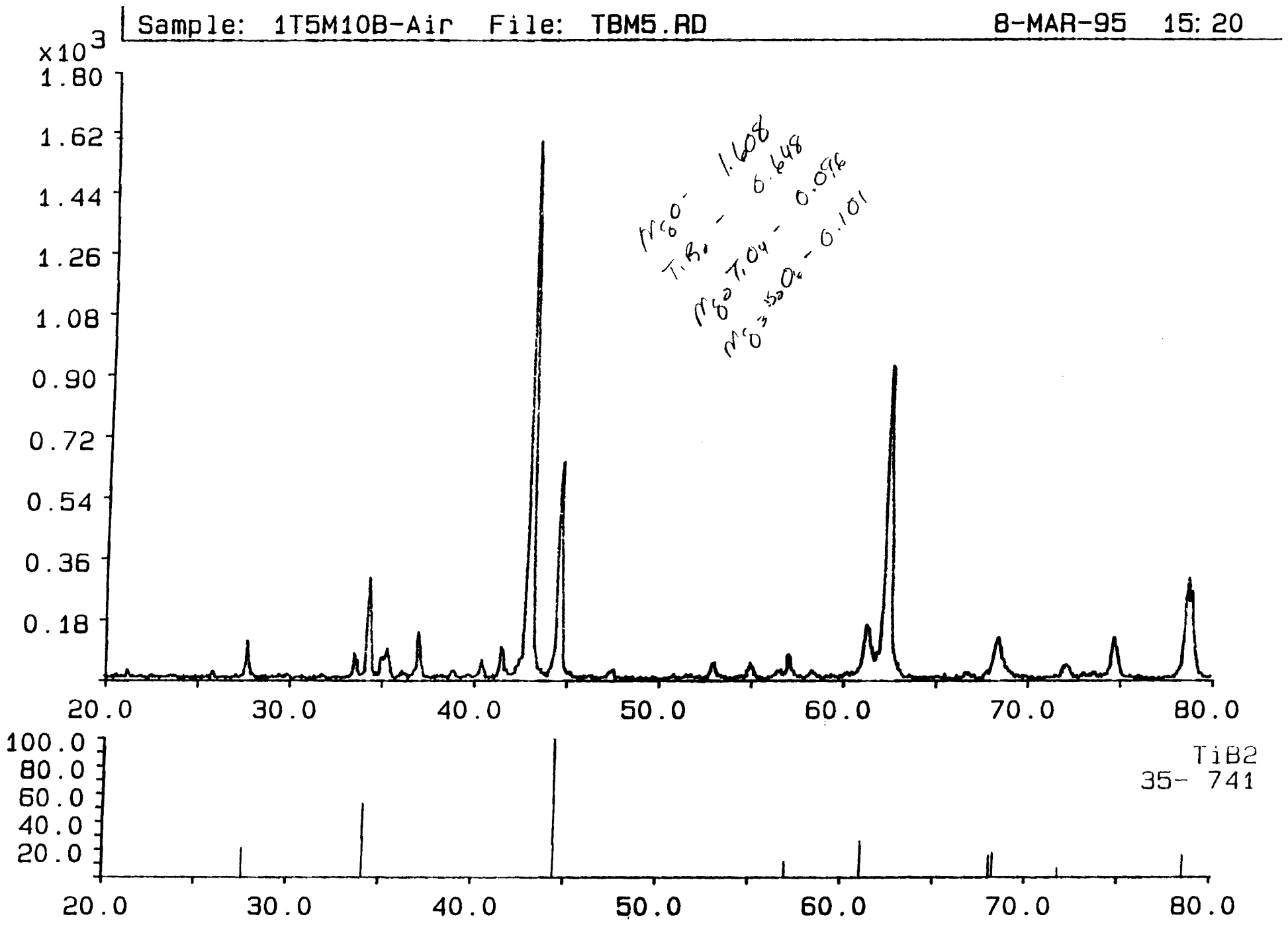
1.62
1.44
1.26
1.08
0.90
0.72
0.54
0.36
0.18
20.0
30.0
40.0
50.0
60.0
70.0
80.0
100.0
80.0
60.0
40.0
20.0
TiB2
35- 741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1.62
1.44
1.26
1.08
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0.72
0.54
0.36
0.18
20.0
30.0
40.0
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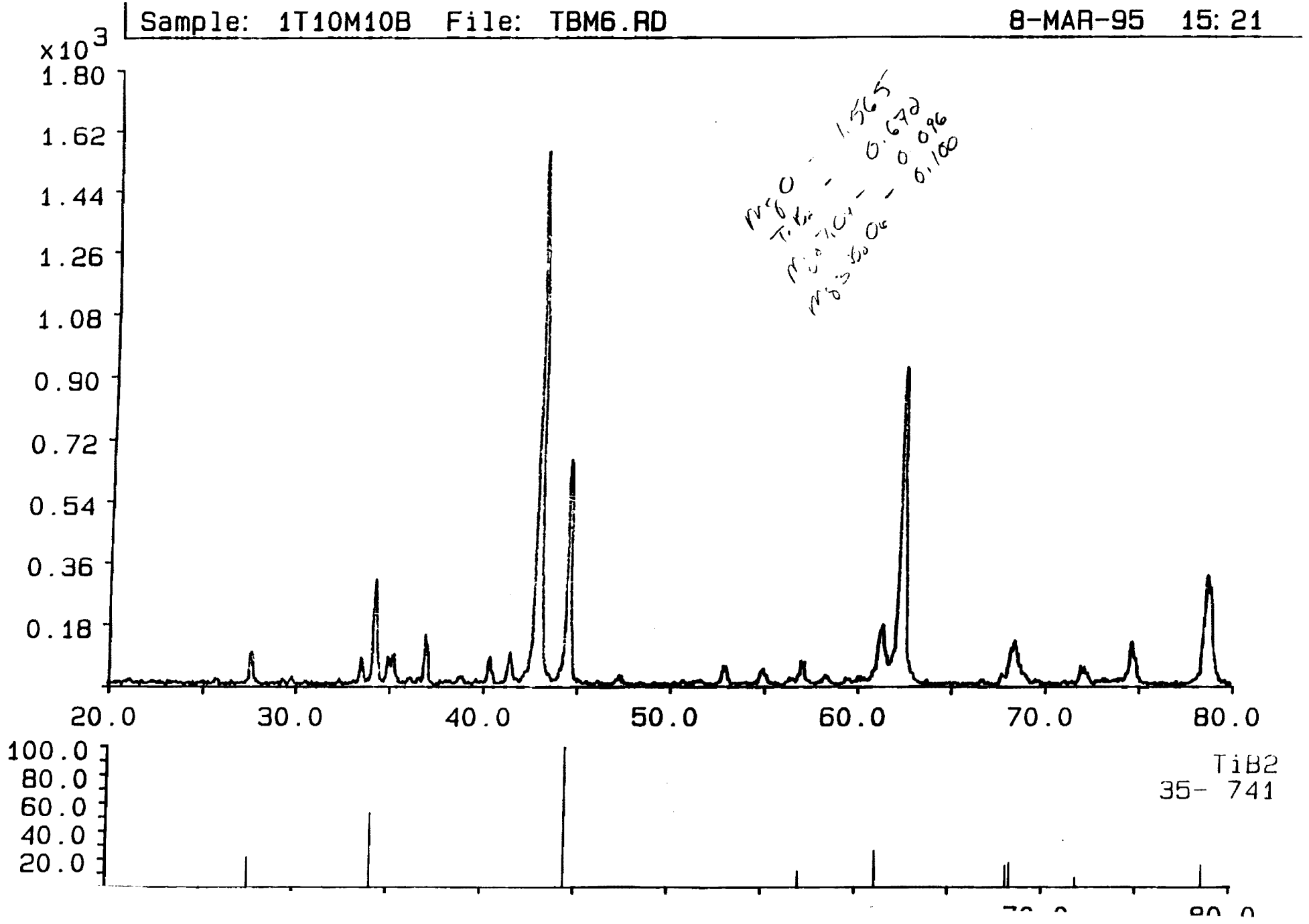
70.0
80.0
100.0
80.0
60.0
40.0
20.0
TiB2
35- 741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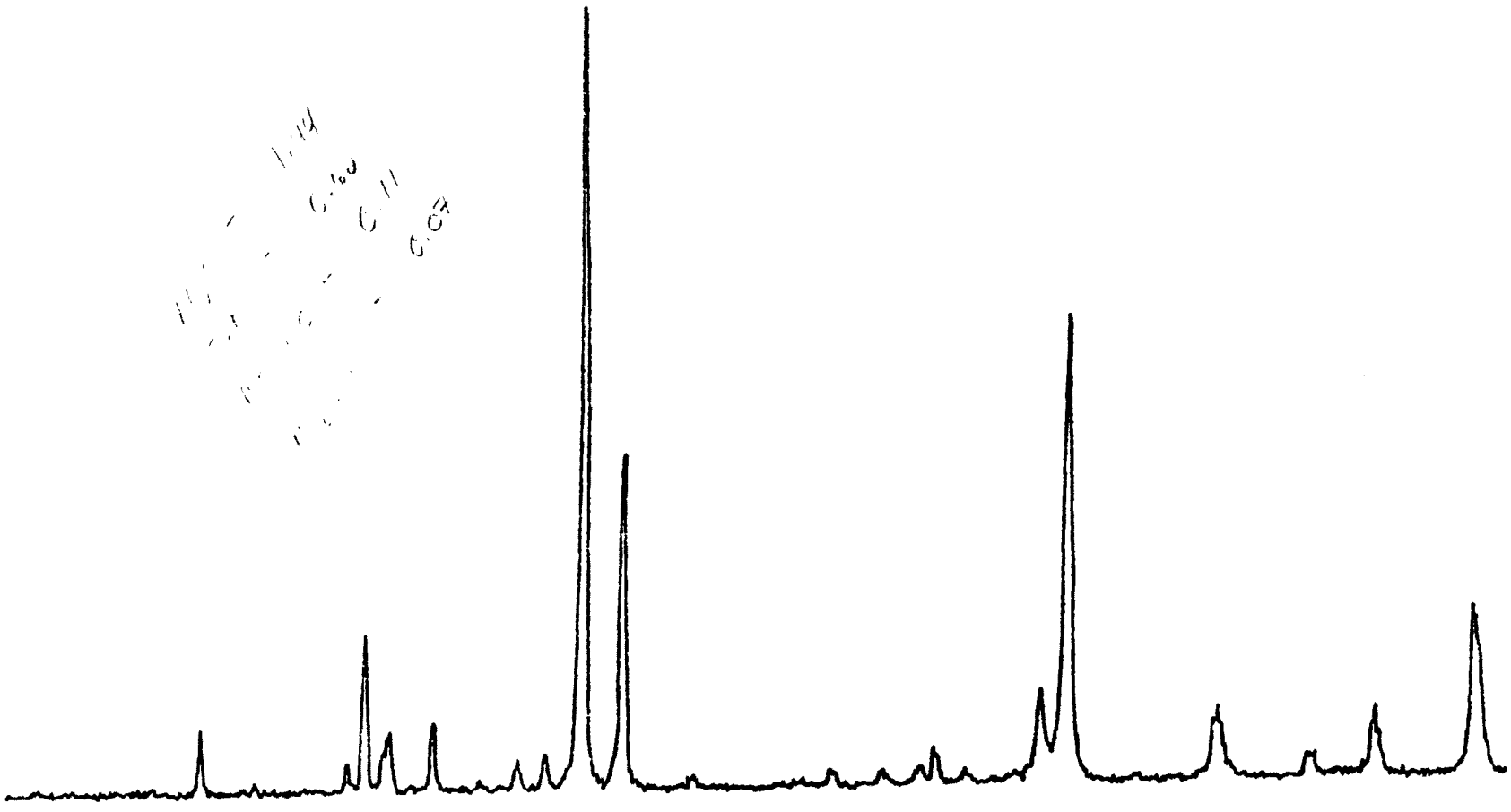
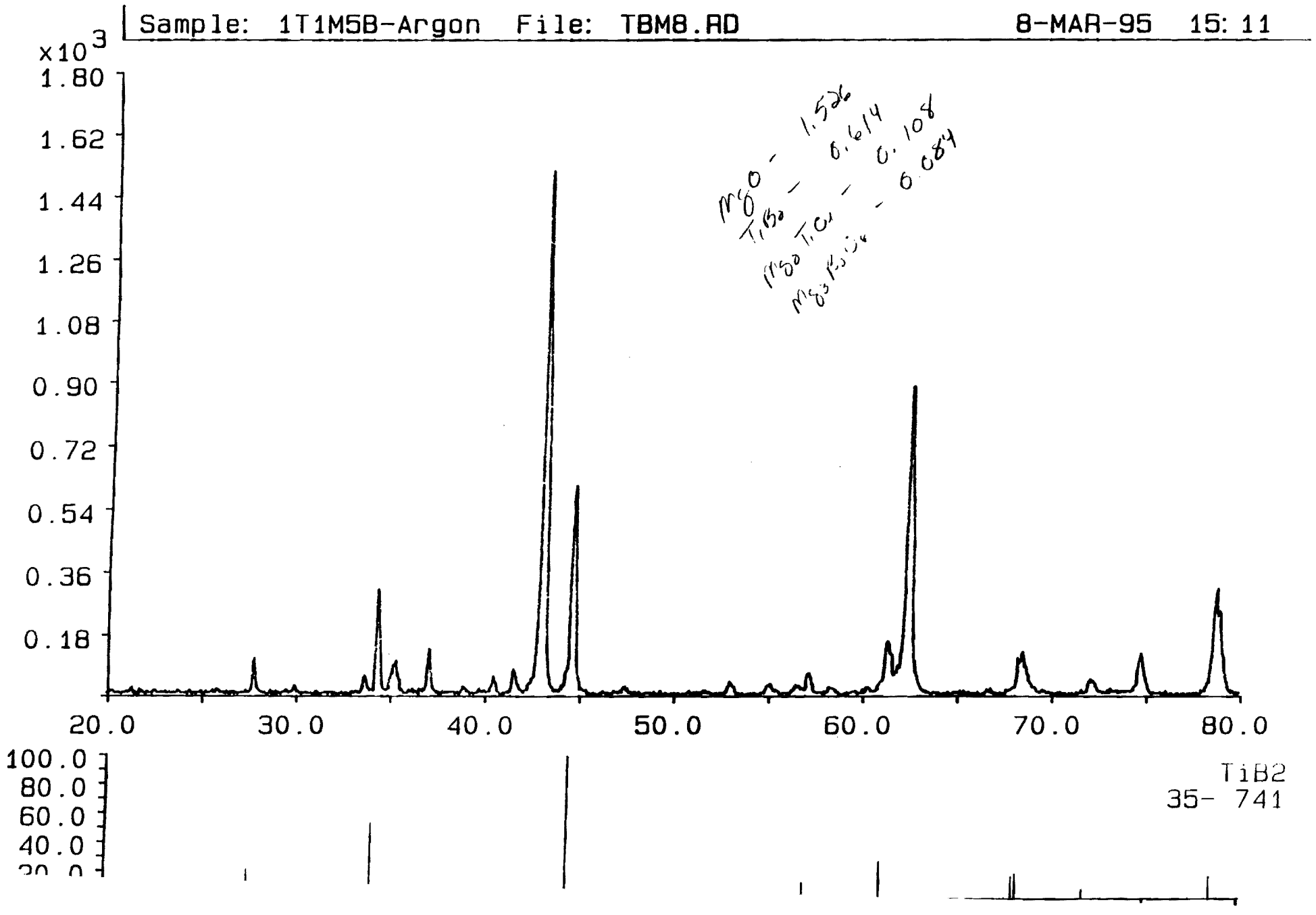
1.62
1.44
1.26
1.08
0.90
0.72
0.54
0.36
0.18
20.0
30.0
40.0
50.0
60.0
70.0
80.0
100.0
80.0
60.0
40.0
20.0
TiB2
35- 741

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8-MAR-95 15:11
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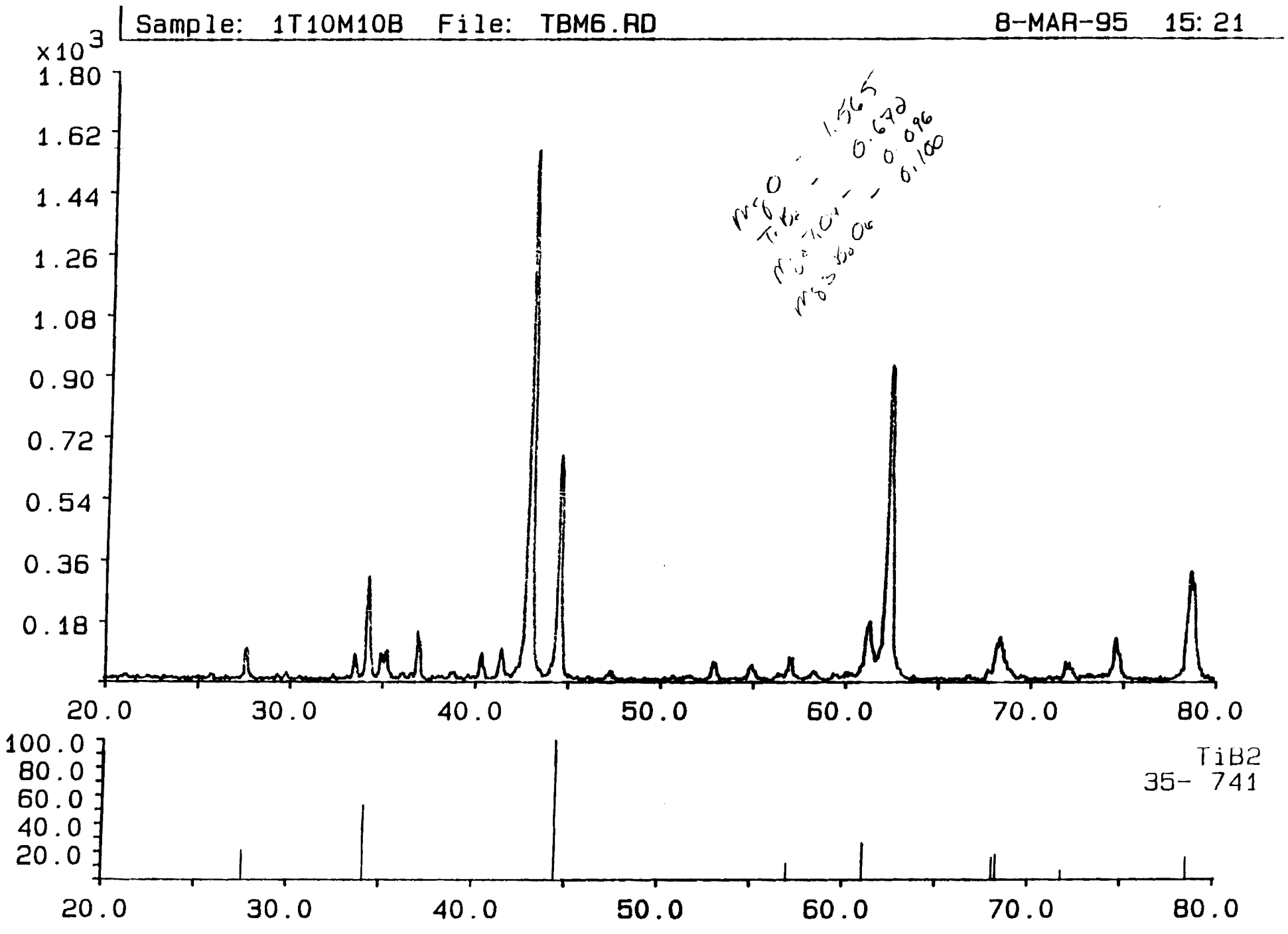
1.62
1.44
1.26
1.08
0.90
0.72
0.54
0.36
0.18
20.0
30.0
40.0
50.0
60.0
70.0
80.0
100.0
80.0
60.0
40.0
TiB2
35- 741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8-MAR-95 15:21
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1.80
1.62
1.44
1.26
1.08
0.90
0.72
0.54
0.36
0.18
20.0
30.0
40.0
50.0
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60.0
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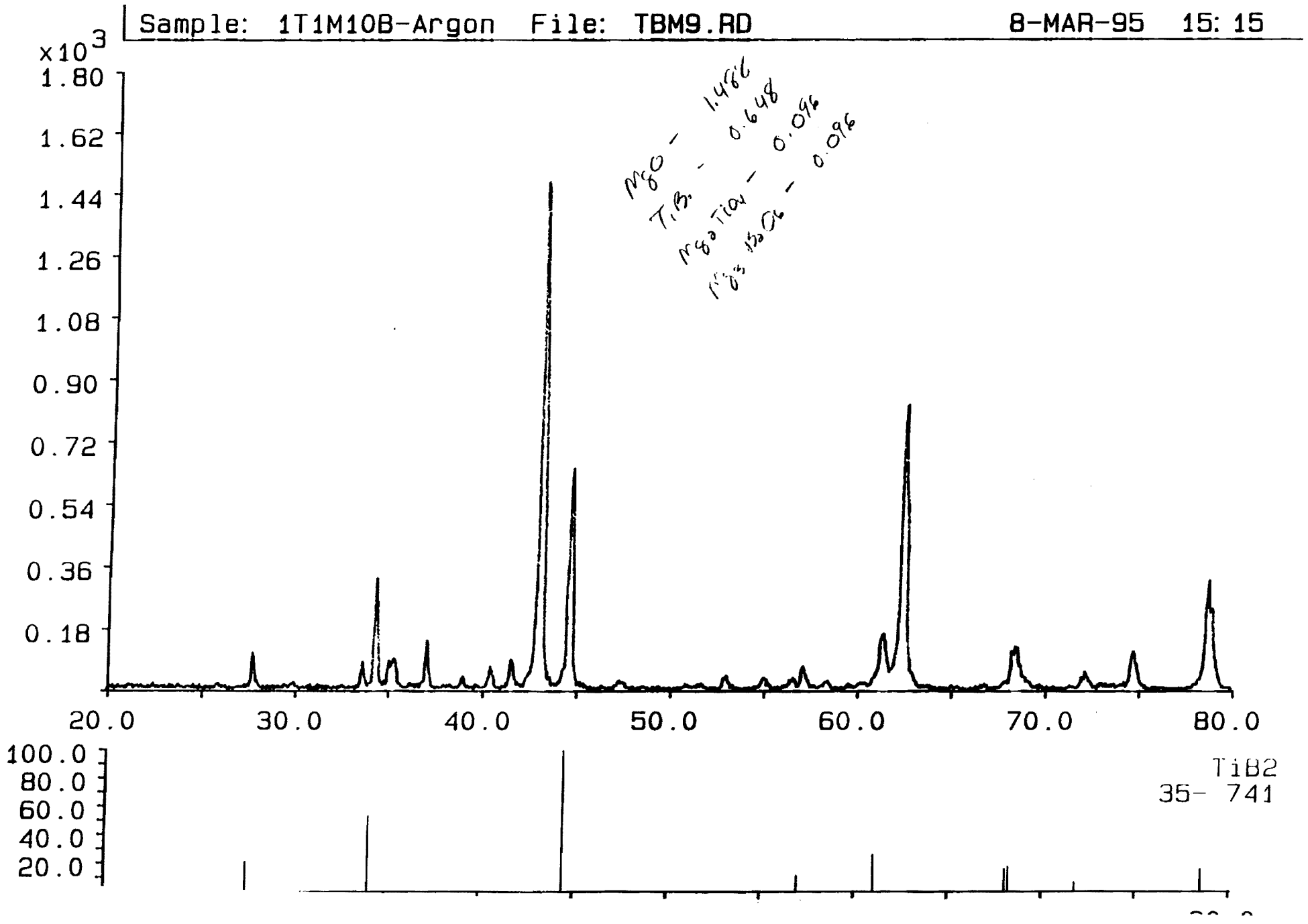
20.0
TiB2
35- 741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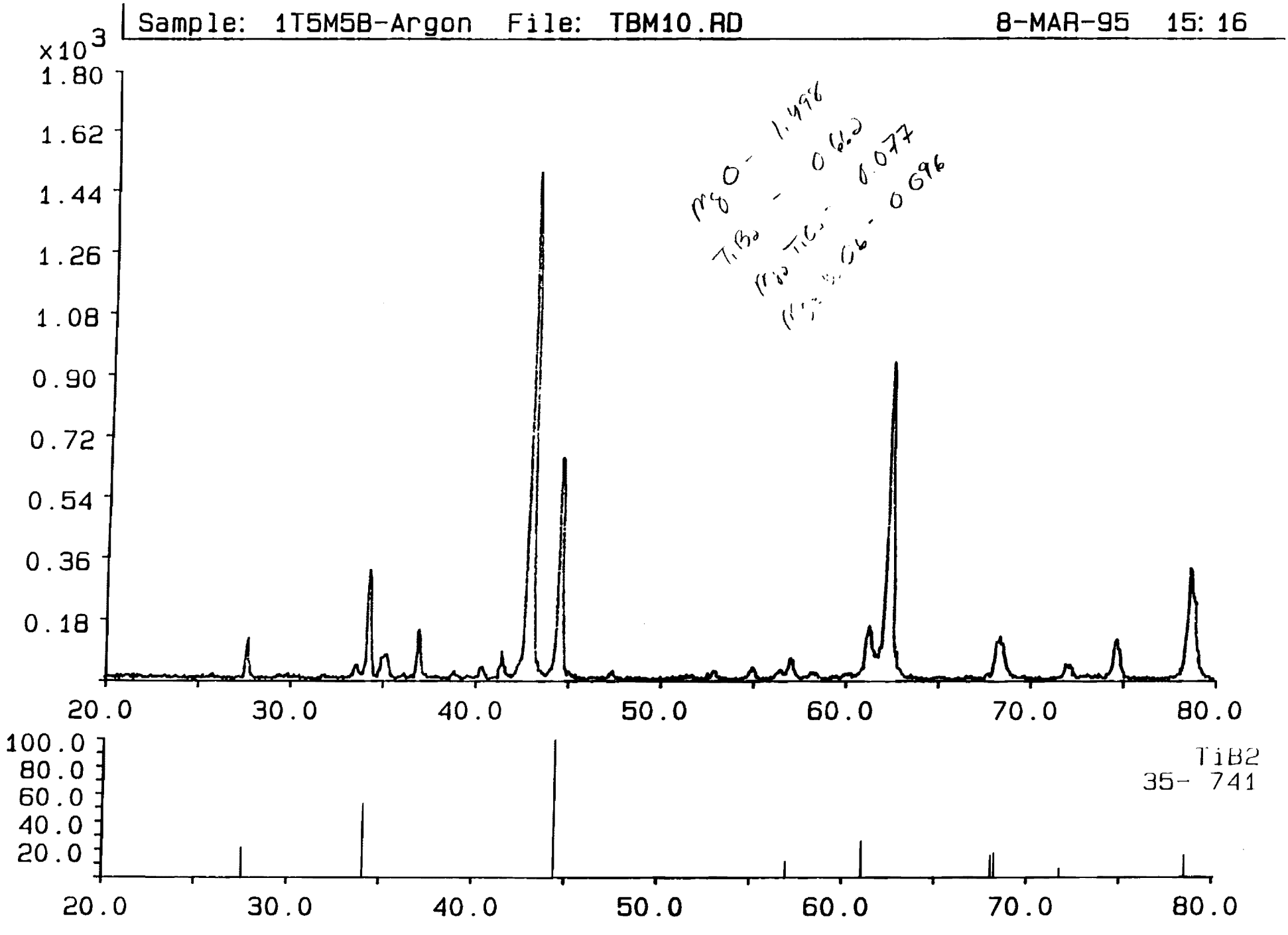
1.62
1.44
1.26
1.08
0.90
0.72
0.54
0.36
0.18
20.0
30.0
40.0
50.0
60.0
70.0
80.0
MgO - 1.486
TiB2 - 0.648
MgTiO4 - 0.096
Mg3B2O6 - 0.096
100.0
80.0
60.0
40.0
20.0
TiB2
35- 741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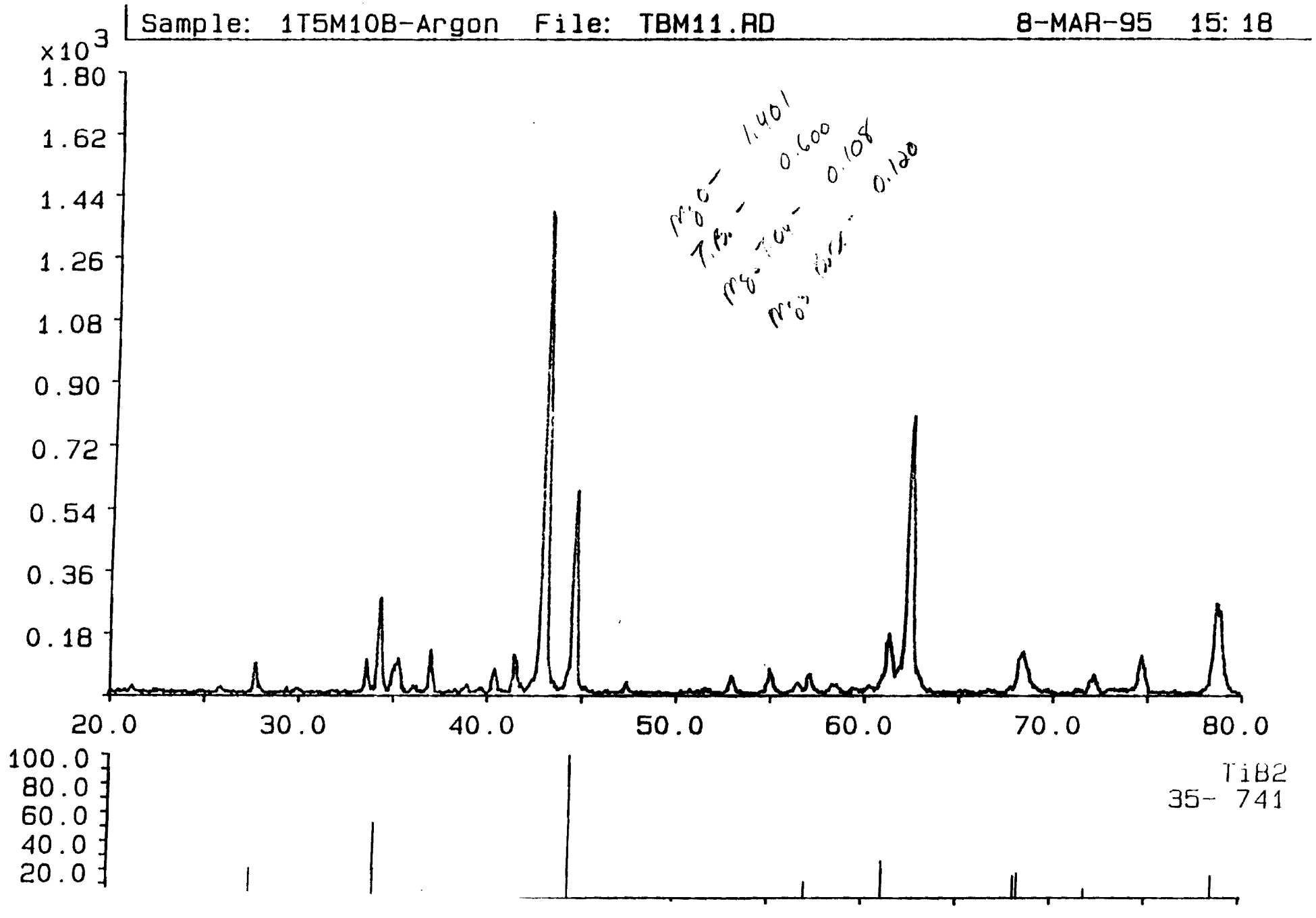
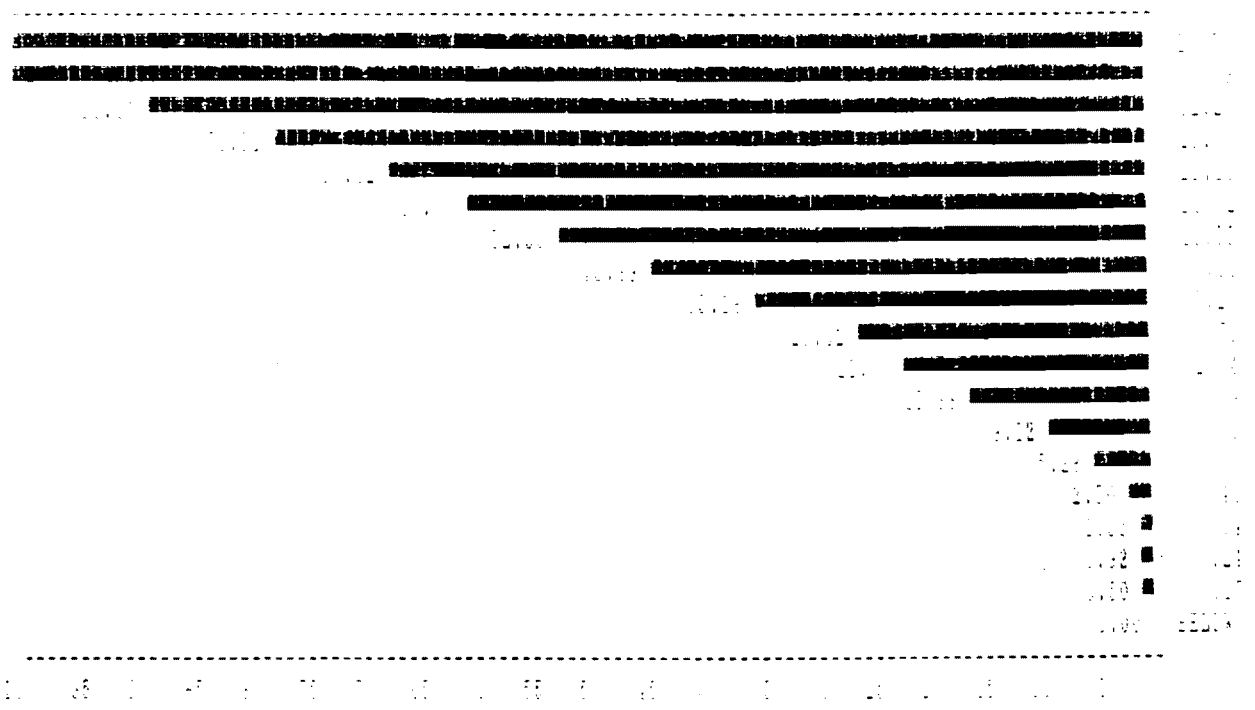
1.44
1.26
1.08
0.90
0.72
0.54
0.36
0.18
20.0
30.0
40.0
50.0
60.0
70.0
80.0
100.0
80.0
60.0
40.0
20.0
TiB2
35- 741


Sample: 1T5M10B-Argon File: TBM11.RD 8-MAR-95 15:18
x10 3
1.80
1.62
1.44
1.26
1.08
0.90
0.72
0.54
0.36
0.18
20.0
30.0
40.0
50.0
60.0
70.0
80.0
100.0
80.0
60.0
40.0
20.0
TiB2
35- 741

PRESSURE VERSUS LOAD

ACTUAL PSI

INDICA PRESSURE	TONS	1"	2"	3"	4"
100	0.8	2024	506	225	127
200	1.6	4049	1012	450	253
300	2.4	6073	1518	675	380
400	3.2	8098	2024	900	506
500	4.0	10122	2531	1125	633
1000	8.0	20245	5061	2249	1265
1500	11.9	30367	7592	3374	1898
2000	15.9	40489	10122	4499	2531
2500	19.9	50611	12653	5623	3163
2890	23.0	58507	14627	6501	3657
3000	23.9	60734	15183	6748	3796
3500	27.8	70856	17714	7873	4428
4000	31.8	80978	20245	8998	5061
4500	35.8	91100	22775	10122	5694



Samples

Quarterly report for Fall '94

Venkatesh Sundaram **Dec. 5, 1994**

Introduction

The goal of the project is to synthesize TiB_2 using a magnesium thermite reaction and also to understand the reaction mechanism. The starting materials for the reaction are Magnesium powder, Boron oxide (B_2O_3 - amorphous) and Titanium oxide (TiO_2 - anatase). The basic reaction in the system can be written as:

$$5Mg + B_2O_3 + TiO_2 \rightarrow 5MgO + TiB_2$$

The product from the reaction is a porous mass consisting of magnesium oxide and titanium diboride with minor amounts of magnesium borate phase formed due to the interaction between MgO and B_2O_3. The magnesium oxide and the borate are removed in the leaching step (by acid) and very fine (sub-micron) pure TiB_2 powder is obtained. The advantages of the thermite process to synthesize titanium diboride include desirable particle size and sinterability and a unique microstructure of the product.

The work done during the last quarter was divided between the school of materials science and GTRI (Baker building and 78H). The experimental work involved in each of these areas is detailed separately. The work this quarter started off at a stage when the literature review for the thesis had just been completed.

Theoretical calculations

The first stage of the work involved analytical calculations to determine the theoretical conditions and thermodynamic parameters associated with the system under consideration. The most important parameter in the reaction is the adiabatic temperature (T_{ad}) which indicates the maximum temperature achieved during the reaction under adiabatic conditions. This temperature is determined theoretically using the enthalpy curves (enthalpy vs. temperature) for the reactants and products. The enthalpy curves for the binary and ternary systems are attached. The adiabatic temperature for the TiB_2 reaction is determined to be 3100 K. Another parameter which will be calculated is the free energies of the various phases formed in the reaction.

Also, enthalpy curves for the aluminum thermite reaction (which yields an alumina - titanium diboride composite) have been plotted to compare the parameters in the aluminum and magnesium thermite reactions.

Experimental work

(1) Thermal analysis

The thermal analysis work was performed in the school of MSE. The work involved mainly differential thermal analysis (DTA) of various powders and powder mixtures. The following systems are considered:

(a) Magnesium + Boron oxide
(b) Magnesium + Titanium oxide
(c) Magnesium + Boron oxide + Titanium oxide
(d) Boron oxide + Titanium oxide

Baseline scans were also done for pure Mg, pure B_2O_3 and pure TiO_2. The two variables being studied are (1) the heating rate and (2) the atmosphere. Two different heating rates of 10 ^{0}C / minute and 50 ^{0}C / minute will be used. The significance of the heating rate is that the hot wire ignition used for the bulk powder production corresponds to a heating rate of about 50 ^{0}C / min. The atmosphere used in the bulk reaction is air. The use of Argon atmosphere in addition to air will provide a measure of the oxygen uptake from the atmosphere and from the oxide reactants during the reaction.

The first step in the DTA runs involved making the two thermocouples, which had to be replaced. The thermocouples will need replacing at regular intervals and the thermocouple fabrication process has been familiarized. Sufficient quantities of S type thermocouple wires are also available.

The DTA was calibrated using a potassium carbonate (K_2CO_3) standard which has a melting temperature of 891 ^{0}C. The DTA signals were accurate up to less than 5 ^{0}C. There still is a control problem in the signal for the first 300 degrees, but this region is not significant for the current experiments.

One set of runs have been completed under flowing Argon at a heating rate of 10 ^{0}C / minute. The DTA traces are attached. Some of the runs were run in duplicate to ensure consistency. It is planned to perform all runs in duplicate. The next phase of the DTA work includes runs at 10 and 50 ^{0}C / minute under air and at 50 ^{0}C / minute under argon.

Other parameters

Another important parameter involved is the mass of the reactants. This si particularly significant in the light of upscaling the process to industrial production levels. There are two alternatives considered at the moment. The first method is to change the weight of the sample in the DTA and study the effect on the resulting trace and the product phases. The second idea involves igniting small quantities (about 25 grams) of the binary and ternary mixtures using hot wire ignition and studying the resulting products and comparing with the product phases in the DTA runs and the bulk process.

There are a number of other parameters that can be varied during the reaction. These include :

(1) Ignition temperature: Room temperature ignition or preheating the reactants)
(2) Stoichiometry: It has been observed that changing the relative amounts of reactants in the bulk reactions results in a change in the amount of borate and titanate phases formed)
(3) Pressure: The effect of gas pressure on the reaction has been studied for other systems. The reactions in our system are performed under ambient pressure.
(4) Nature of reactants: Loose powders or compacted pellets
(5) Particle size of reactants: The effect of particle size on the reaction parameters is well documented for other SHS systems but these cannot be generalized to our system.

The present set of experiments maintains all the above parameters constant. The experimental design at this time is a 2 X 2 grid consisting of two different atmospheres and heating rates. This grid can be expanded to include the effects of other parameters.

(2) Work done in GTRI

The major emphasis in the experimental work done in GTRI has been on the bulk reaction to produce large quantities of the powders. There have been two different materials produced, pure TiB_2 and an Al_2O_3-TiB_2 composite. The various stages of the work are described in detail below.

(a) Powder synthesis using thermite reactions.

The first stage of synthesis involved the setting up of the experiment station. Although the reaction chamber was available, it was in bad shape and had to be fixed. The reaction chamber is a 4' x 4' x 6' tall cubicle with an exhaust fan at the rear, two doors and a Plexiglas viewing window. The base of the chamber is lined with refractory bricks and all the inner surfaces are lined with insulation.

The first step in the process is powder mixing. The reactant powders are weighed in the appropriate stoichiometry and then mixed thoroughly to obtain a homogenous powder mixture weighing 600 grams. This mixture is then placed in a slip cast silica crucible such that there is a uniform layer of powder. The crucible is then placed inside the chamber and the powder is ignited with the help of a resistance heated wire. There is another empty crucible on the bottom crucible to contain the reaction and also an insulating lid to prevent nitriding.

The silica crucibles were slip cast in the laboratory. The slip casting molds were made out of plaster into the desired shapes and then the slurry was poured in to make the slip cast silica crucible. These crucibles were then baked in an argon furnace at 1200 ^{0}C. A total of about 30 crucibles have so far been cast and more will be cast when required. It is observed that the crucibles tend to crack after about 15-20 reactions.

After the crucibles are removed from the reaction chamber, the porous product mass is removed and then weighed before being bottled. A small amount of the product around the hot wire has

to be discarded to prevent contamination. So far, I have been involved in the production of about 100 pounds of composite powder and about 50 pounds of pure TiB_2.

(b) X-ray diffraction

The products from the first few composite and pure TiB_2 reactions were analyzed using XRD to check for the phases desired. The composite powder contains only alumina and titanium diboride and does not contain any impurity phases. The product from the magnesium reaction consists mainly of MgO and TiB_2 with a minor amount of magnesium borate. the MgO and the borate will be removed during the leaching step to yield pure TiB_2. The reaction products were also ball milled and the resulting powders were analyzed for any contamination from the milling medium.

At present, samples of the smoke from the reaction are being collected to analyze the particulates in the smoke by XRD and SEM. Also, samples from the powder deposited on the inner surfaces of the crucibles and the hard crust formed in the crucibles after reaction were analyzed using XRD.

(c) Particle size analysis

Particle size analysis was done in the school of MSE using the Microtrac laser particle size analyzer. The powders from the ball milled product were sampled by coning and quartering and then dispersed in water containing a few drops of surfactant (Darvan #7) using an ultrasonic dismembrator. The sample was then loaded into the analyzer and about 4-5 runs were done for each powder to obtain consistent results. The particle size work had to be interrupted for about a month due to a malfunction in the instrument. This problem has been fixed and the analysis will be restarted this week.

(d) SEM

Samples were obtained form the ball milled powders and the as-reacted powders and prepared for SEM examination. Backscatter mode was used to locate foreign particles and heavy elements in the powder sample and the elemental composition was confirmed using EDS. Some samples from attrition milling (done outside Ga. tech) were also examined by SEM/EDS to check for contamination and to assess the feasibility of attrition milling for mass production.

Future work

The current focus is on the DTA runs under argon and air at the two heating rates. The plans for future wok include studying the effect of reactant mass by igniting small amounts (~25g) of the

binary and ternary mixtures. Another aspect that could be researched is the effect of the ignition temperature (room temperature ignition or ignition after preheating).

AEM Project A-9859
12/5-12/9

A. The hot press run was shut down on Monday as a result of the bottom punch collapsing. It was discovered that the base plates were deformed and cracked, causing the surface to be uneven. The plates have been replaced and the hot press is ready to run again. New Kaowool board has been cut and new Kaowool paper has been ordered to place between the bricks.

B. The leaching set-up has been moved to 118 in Baker as a result of the lack of hood space. All of the needed equipment, except two funnels, is ready to use, including the probes for the PH meter.

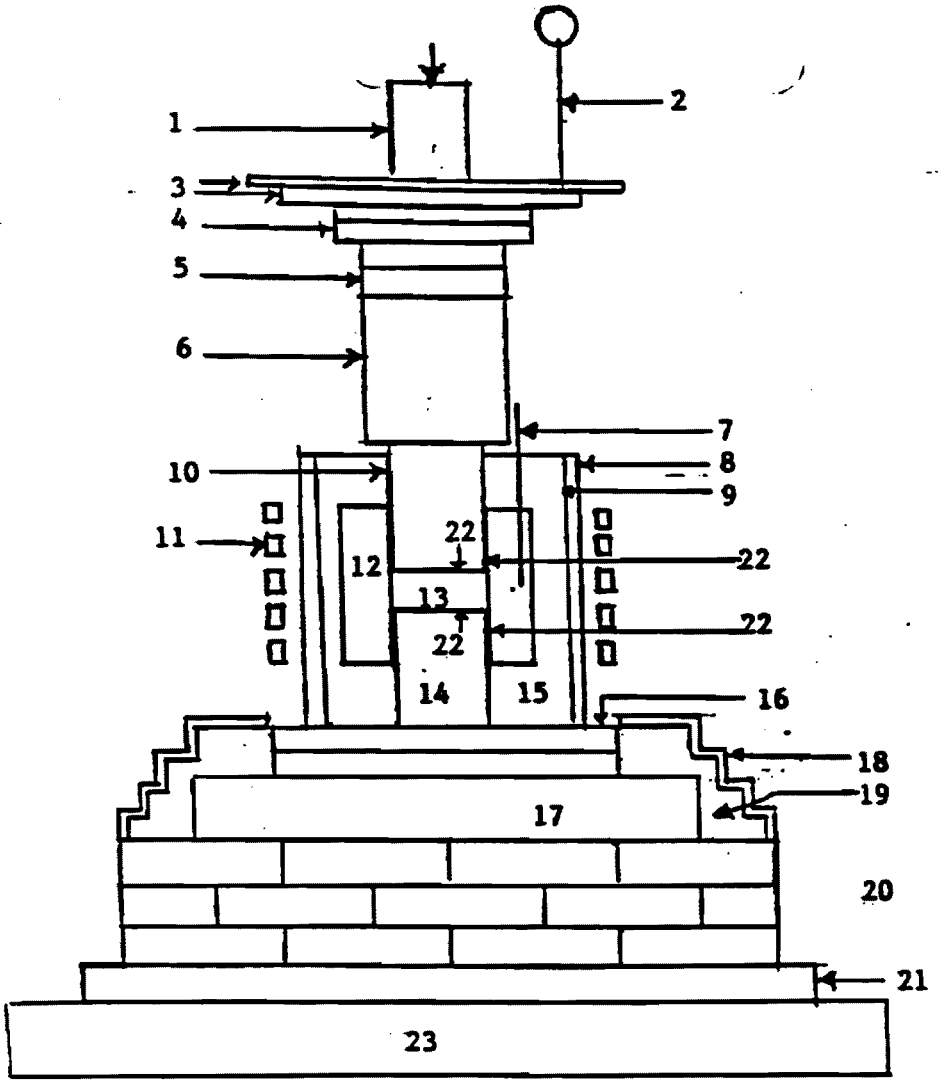
C. The new graphite has arrived from Poco. The punches are 3" exactly and the dies have been machined to 3.060" to allow for the grafoil and slippage. The graphite is marked XT and will be stored in a separate cabinet in 78H.

D. Five pounds of Magnesium flake has arrived.

E. Union Process has returned the remainder of the unmilled composite powder. It was received Friday and has yet to be weighed.

F. Four small cans of atomized Al were received from Alcoa. These were grade 1641L, lot #21159 .

G. There was a five pound container of Mg turnings received. It is in room 118 in the Baker building.



Schematic showing hot press set-up

1	Piston
2	Gage
3	Steel plate & bar
4	4"d pyrographite (two)
5	3"d pyrographite (two)
6	4"d graphite plunger
7	Thermocouple (type "s")
8	Alumina riser sleeve
9	Kaowool sleeve
10	3"d graphite plunger
11	Cu coil
12	6"d graphite die
6	6"d graphite die
13	Powder
14	3"d graphite plunger
15	Alumina bubbles/carbon
16	SiC plate (two)
17	Refractory bricks
18	Kaowool boards
19	Alumina bubbles/kaowool
20	Refractory bricks
21	Steel plate
22	Graphoil
23	Steel frame base

AEM Weekly Report 1/23/95-1/27/95

1. Leaching Study

	1st (ml) (pH)	2nd (ml)	HNO_3 (ml)	Dry mass (g)	Sulfur (ml)	XRD result	
1	900 (2.0)	96	996	89.6		* TiO_2 & minimal borates	
2	910 (2.0)	63	(973)	82.5	21 cold	* TiO_2 & minimal borates	
3	929 (2.0)	60	989	95.8	16 cold	* TiO_2 & minimal borates	
4	956 (2.0)	45	1001	95.0	16 cold		
5	944 (2.0)	70	1014	99.8	16 cold	* TiO_2 & minimal borates	
6	978.5 (2.0) Low pH accident	50	1028.5	101.0	16 cold	* Enhanced TiO_2 & unidentifiable borates	
7	939.5 (2.0)	28.5	968	100.6	16 cold	TiO_2; reduced borates (disappeared after sulfur)	
8	951 (2.0)	15	966	97.3	18 cold	TiO_2, minimal borates	
9	740 (3.0) Early cut	73	813	213	31 cold	* Appreciable borates	
10	828 (3.0) Stayed longer	95	923	133*	42 (45°C)	Fine part: best Coarse: MgO	
11	500 (3.0) Early cut	330	830	142*	143 (45°C)	Bad, MgO peaks are too much obvious	

12	944 (2.5)	41	985	168.4 *100g	202 (50-90°C)	Appreciable borates with normal MgO; worth while to check after sulfur wash	
13	904 (2.5)	23	927	93 *91.8	41 (50-90°C)	As good as #10 fine part	
14	923 (2.5)	25	948	*91.7		Much reduced borates than #12 & #15	
15	864 (2.5)	63	927	*97.9		Appreciable borates with normal MgO	
16	716 (3.0)	184	900	109.8 *99.5	200 50-90C		
17	824 (3.0)	71	895	109.4 *87.6	200 50-90C		
18	806 (3.0)	100	906	97.5	90 50-90C		
19	780 (3.0)	103	883	110.4	150 50-90C		
20	(2.5)	planned					
21	(2.5)	planned					
25	715 (2.5)	48	763	93.90	20 70-83C		
26	930 (2.5)	50	980	82.14	15 56-79C		
M1	920 (2.5)	35	955	90.90	30 55-75C		
27	914 (2.5)	13	927	93.10	10 55-75C		
28	910 (2.5)	53	963	101.8	152 50-85C		
29	800 (2.5)	99	899	99.90	63 50-85C		

30	925 (2.5)	31	956	93.50	5 56-75C		
31	885 (2.5)	50	935	83.30	20 55-75C		
32							
33							
34							

Asterisk (*) indicates data obtained after sulfur washing. Unmarked values of dry mass and unmarked remark of XRD results were obtained after second nitric acid washing.

TIB2 HOT PRESS

PARAMETERS

RUN	TYPE POWDER	MASS (g)	DRY-PRESS (PSI)	FINAL-PRESS (PSI)	FINAL TEMP (C)	RAMP TIME (MIN)	SOAK TIME (HOURS)	THERMOCOUPLE TYPE
1	TiB2	339.0	3374	3374	1580	28	4.16	S
2	TiB2	340.0	4499	4499]	1580	25	6:15	S
3	TiB2	340.0	4499	4499	1580	60	4.12	S
4	TiB2	340.0	4499	6501	1580	145	4:20	S
5	TiB2	340.0	4499	6501	1580	148	5:45	S
6	TiB2	340.0	5174	6074	1670/1640	98	4:00	B
7	TiB2	340.0	5062	5062	1655	34	0:14	B

TIB2 HOT PRESS

DISK DATA

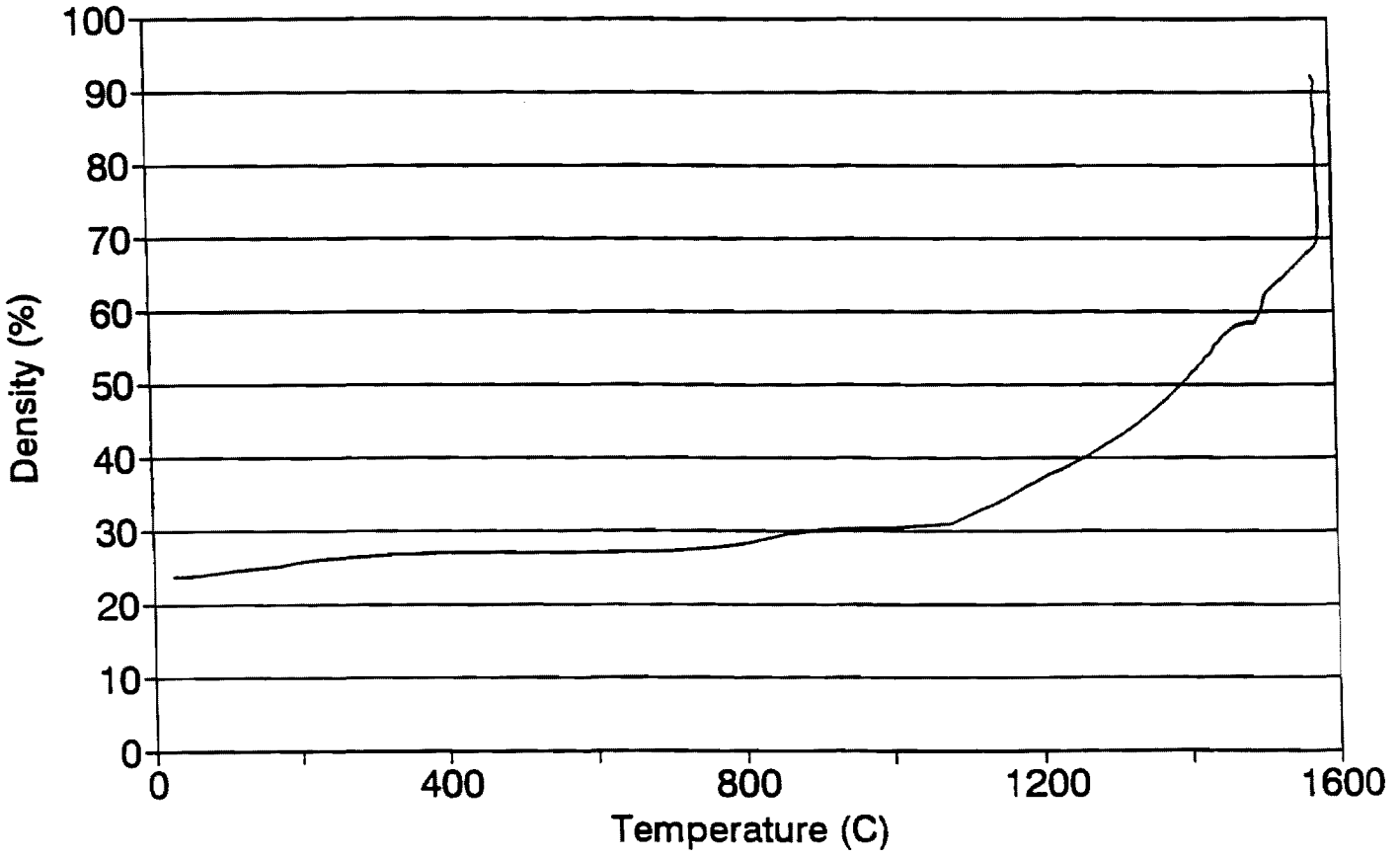
DISK	DIMENSIONS DIAMETER (IN)	DIMENSIONS THICKNESS (IN)	GROSS MASS (g)	NET MASS (g)	THEORETICAL DENSITY (G/CM3)	TRUE DENSITY (G/CM3)	PERCENT DENSE
1	3.0	0.468	339.0	287.65	4.51	4.18	92.70
2	3.0		340.0	234.32	4.51	4.33	95.96
3	3.0	0.534	340.0	248.02	4.51	4.13	91.60
4	3.0	0.484	340.0	236.80	4.51	4.16	92.30
5	3.0	0.504	340.0	227.80	4.51	4.23	93.7
6	3.0	0.476	340.0	241.85	4.51	4.35	96.40
7	3.0	0.409	295.5	154.59	4.51	4.15	91.91

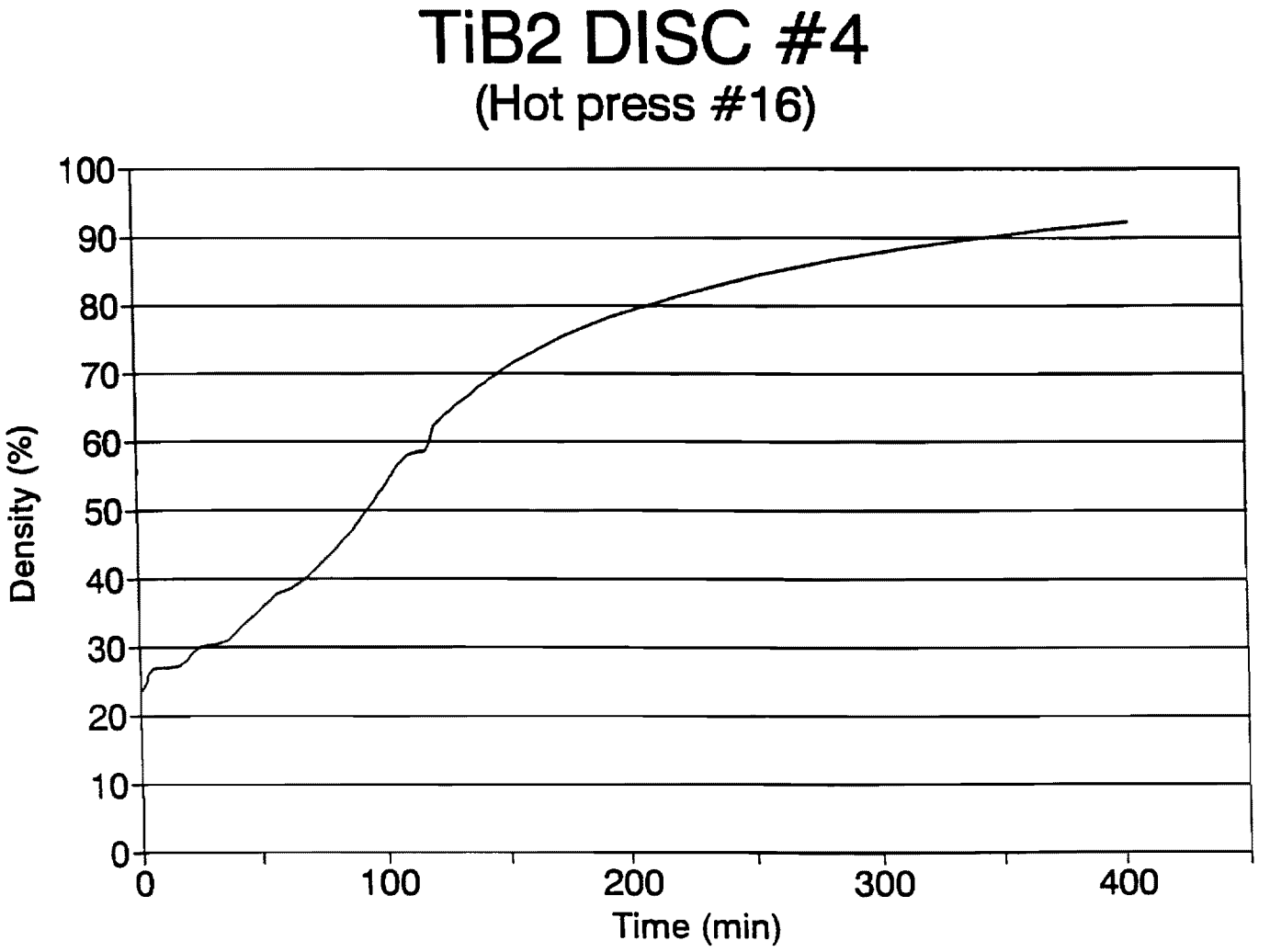
NOTES:

Disk 6 - Alumina sheath broke, type "B" thermocouple failed
temp. reduced to 1640, run completed
Disk 7 - Power failure twice, run incomplete

TiB2 DISC #4

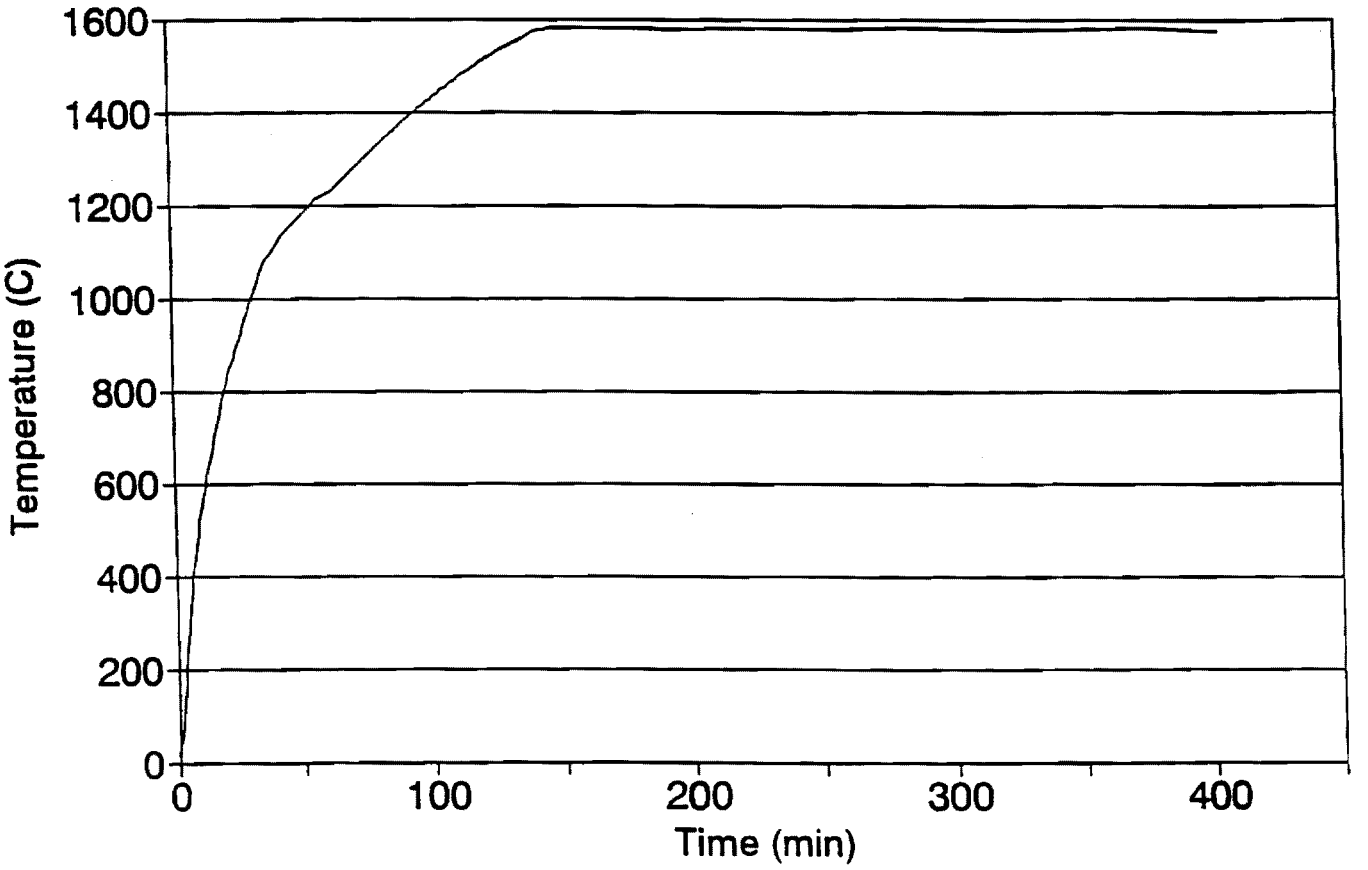
(Hot press #16)




TiB2 DISC #4
(Hot press #16)
Density (%)
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
Time (min)

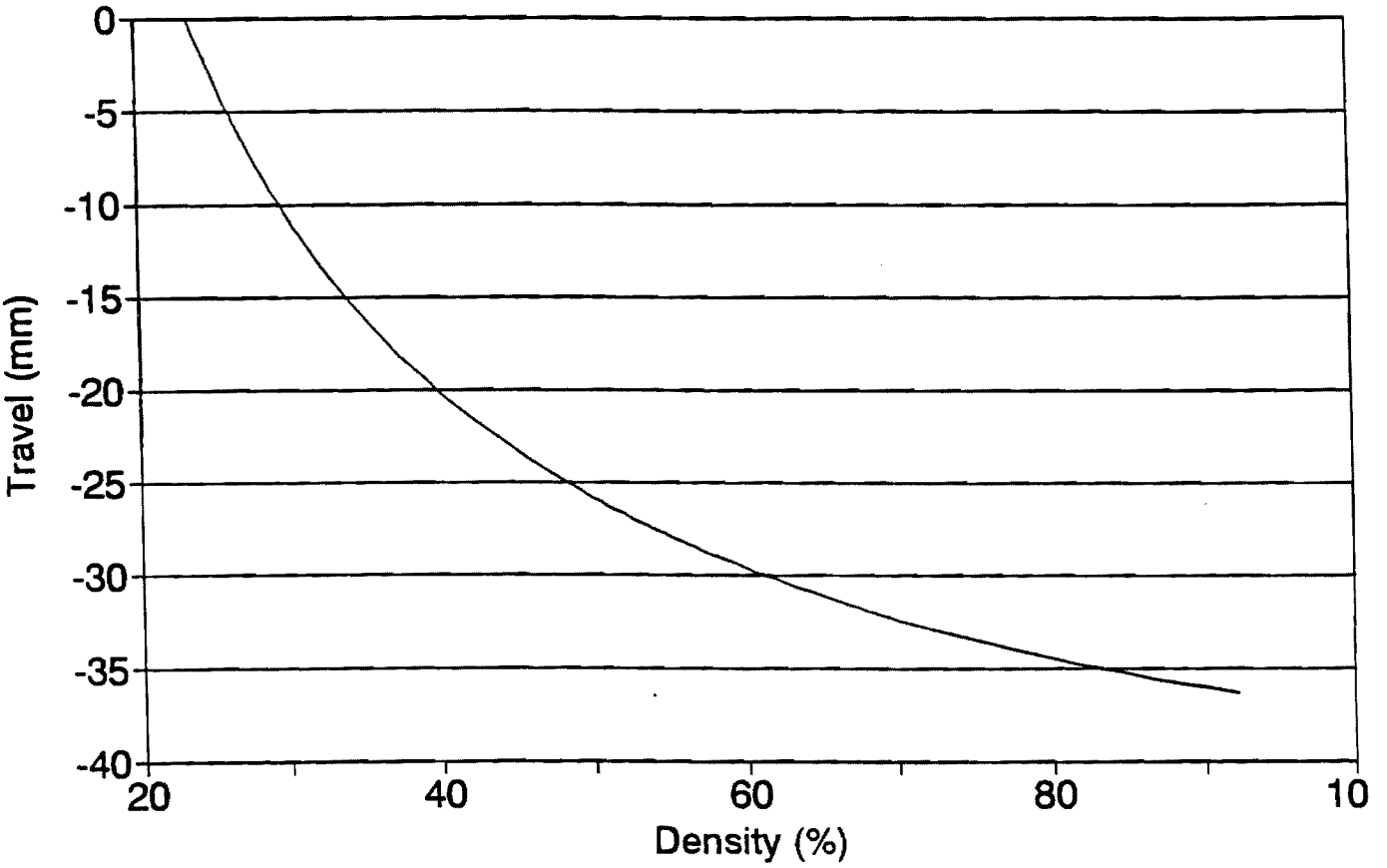
TiB2 DISC #4

(Hot press #16)



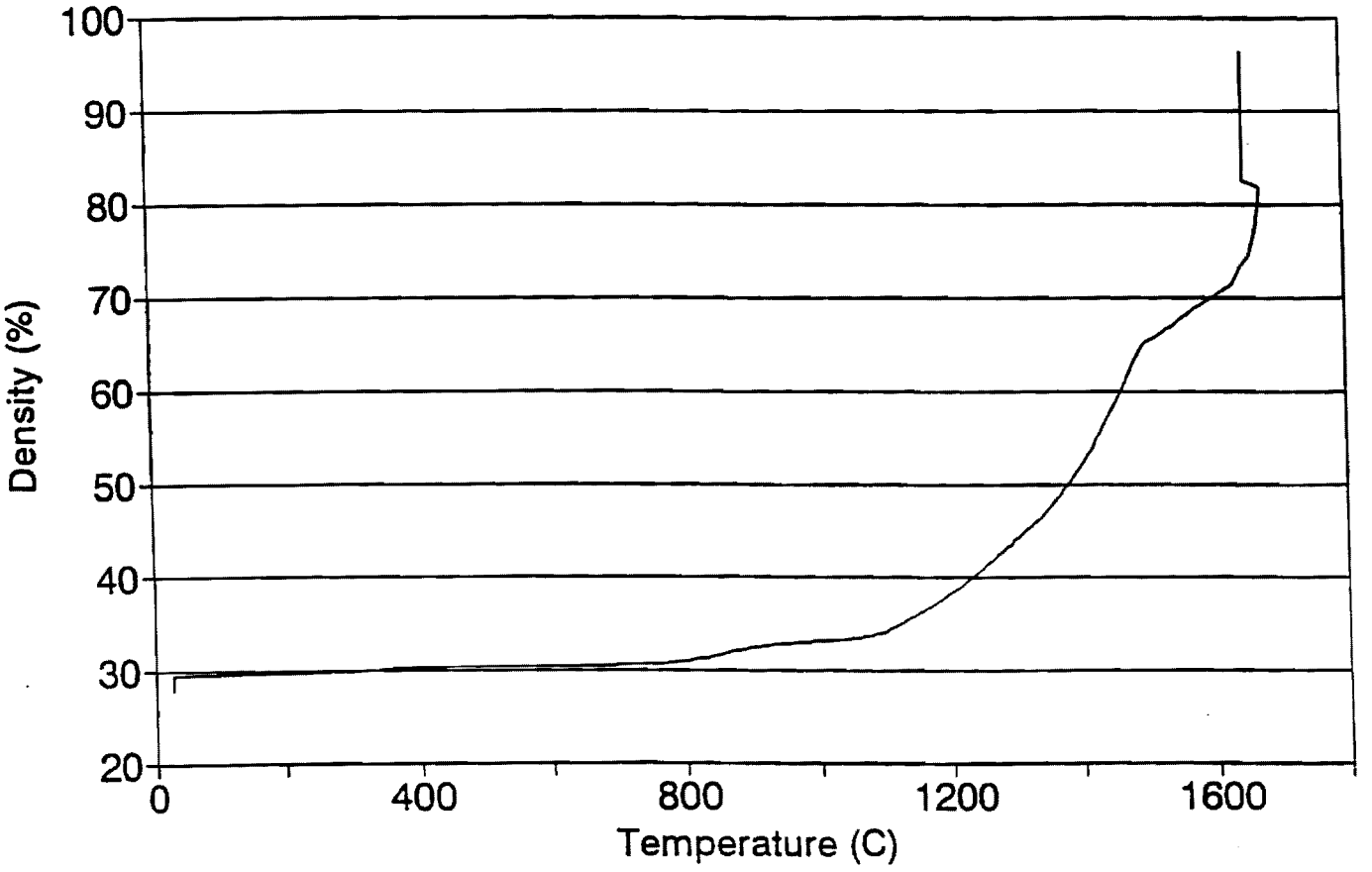
TiB2 DISC #4

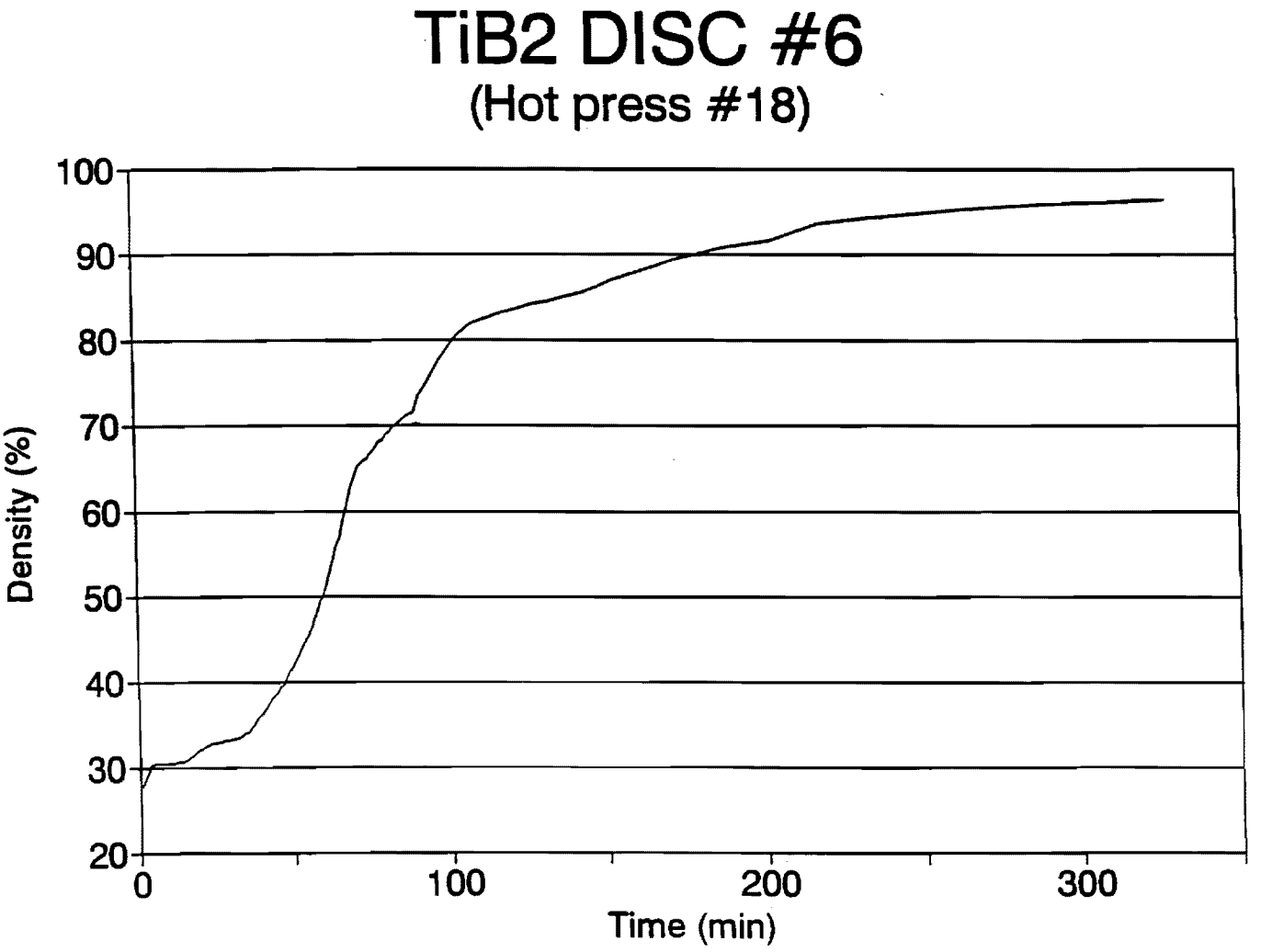
(Hot press #16)



TiB2 DISC #6

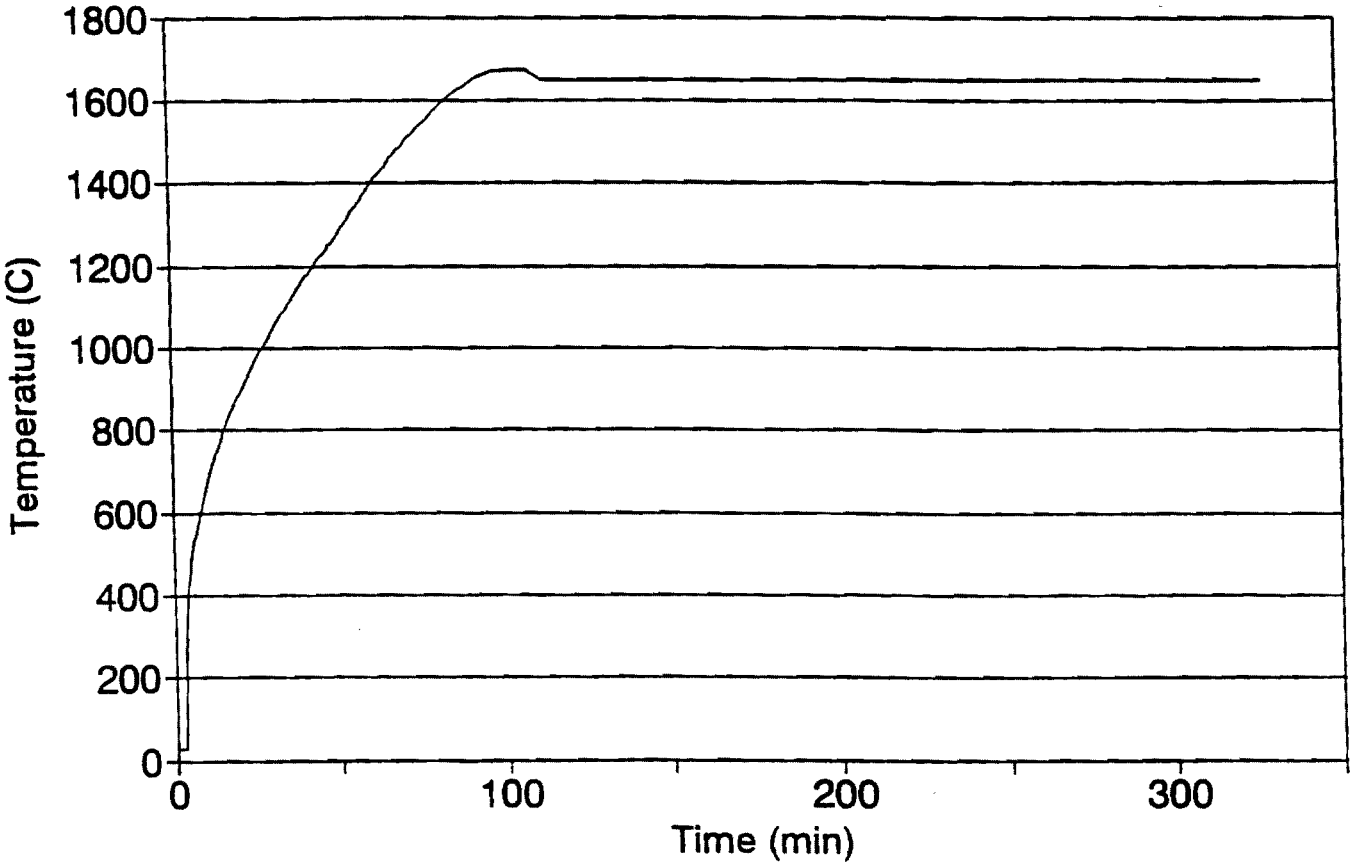
(Hot press #18)




TiB2 DISC #6
(Hot press #18)
Density (%)
100
90
80
70
60
50
40
30
20
0
100
200
300
Time (min)

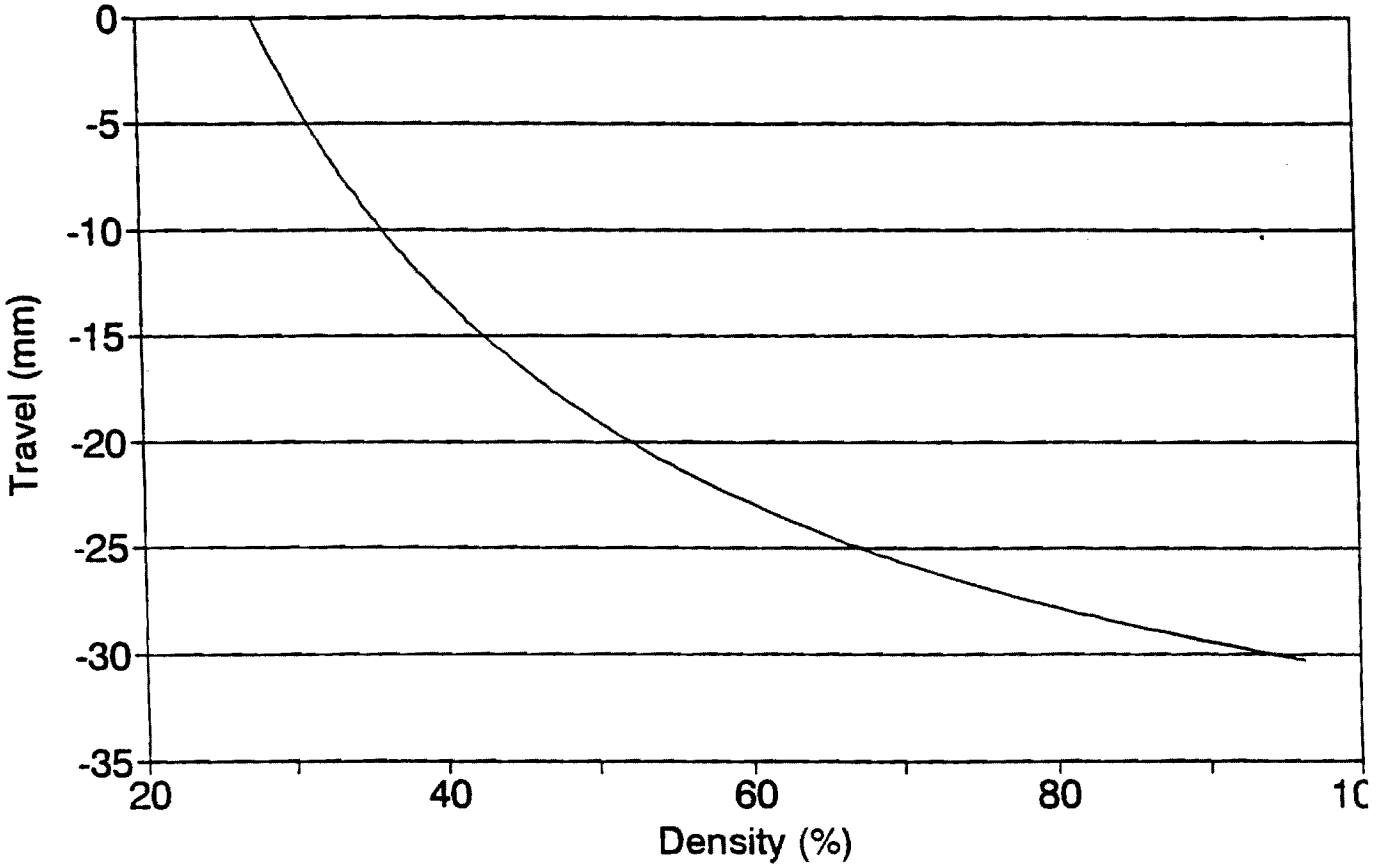
TiB2 DISC #6

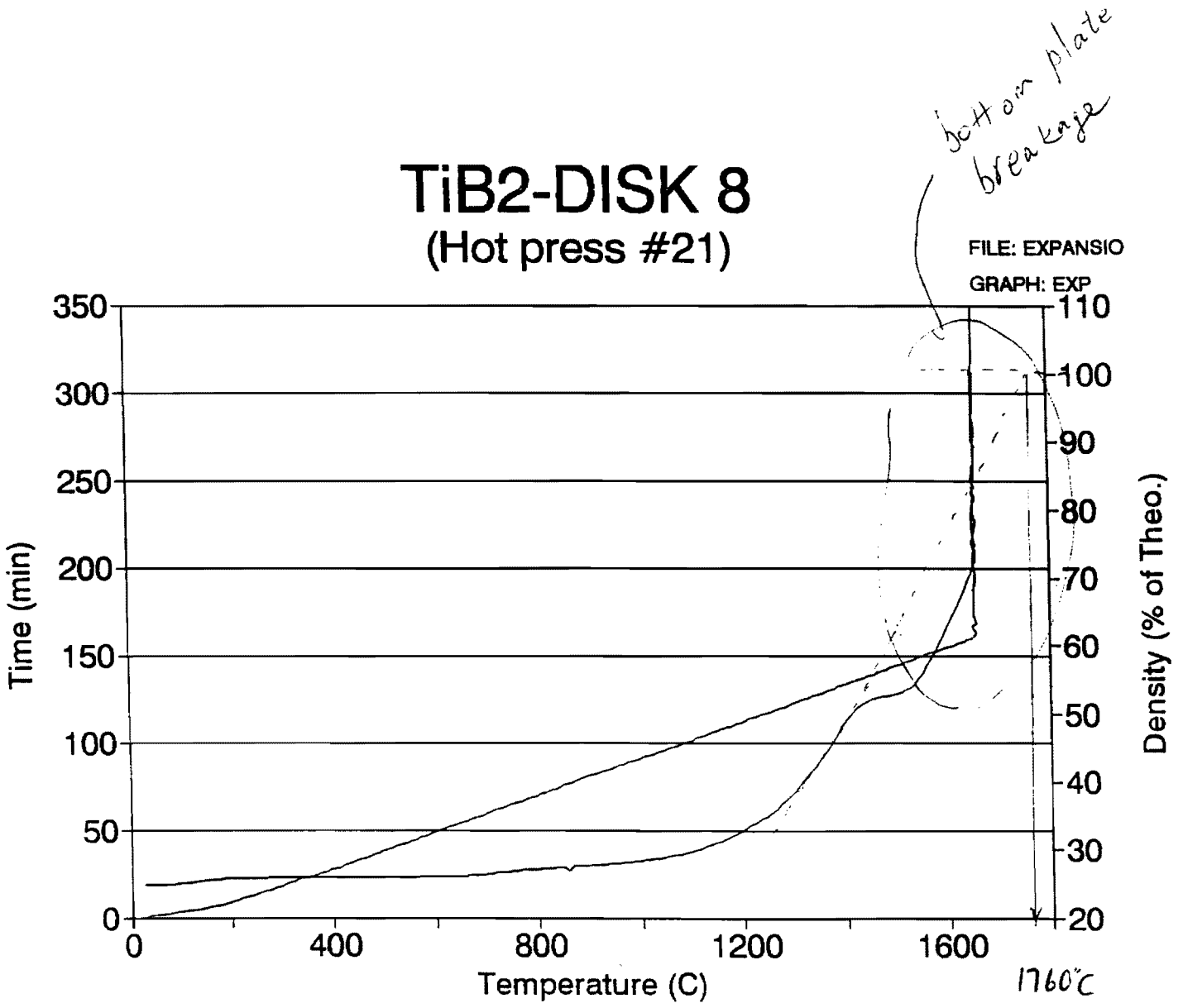
(Hot press #18)



TiB2 DISC #6

(Hot press #18)




TiB2-DISK 8
(Hot press #21)
bottom plate breakage
FILE: EXPANSIO
GRAPH: EXP
Time (min)
Density (% of Theo.)
Temperature (C)
1760°C
0
50
100
150
200
250
300
350
20
30
40
50
60
70
80
90
100
110
0
400
800
1200
1600

Characterization of the First TiB_2 Electrode after Service

By Hyunho Shin

February 17, 1995

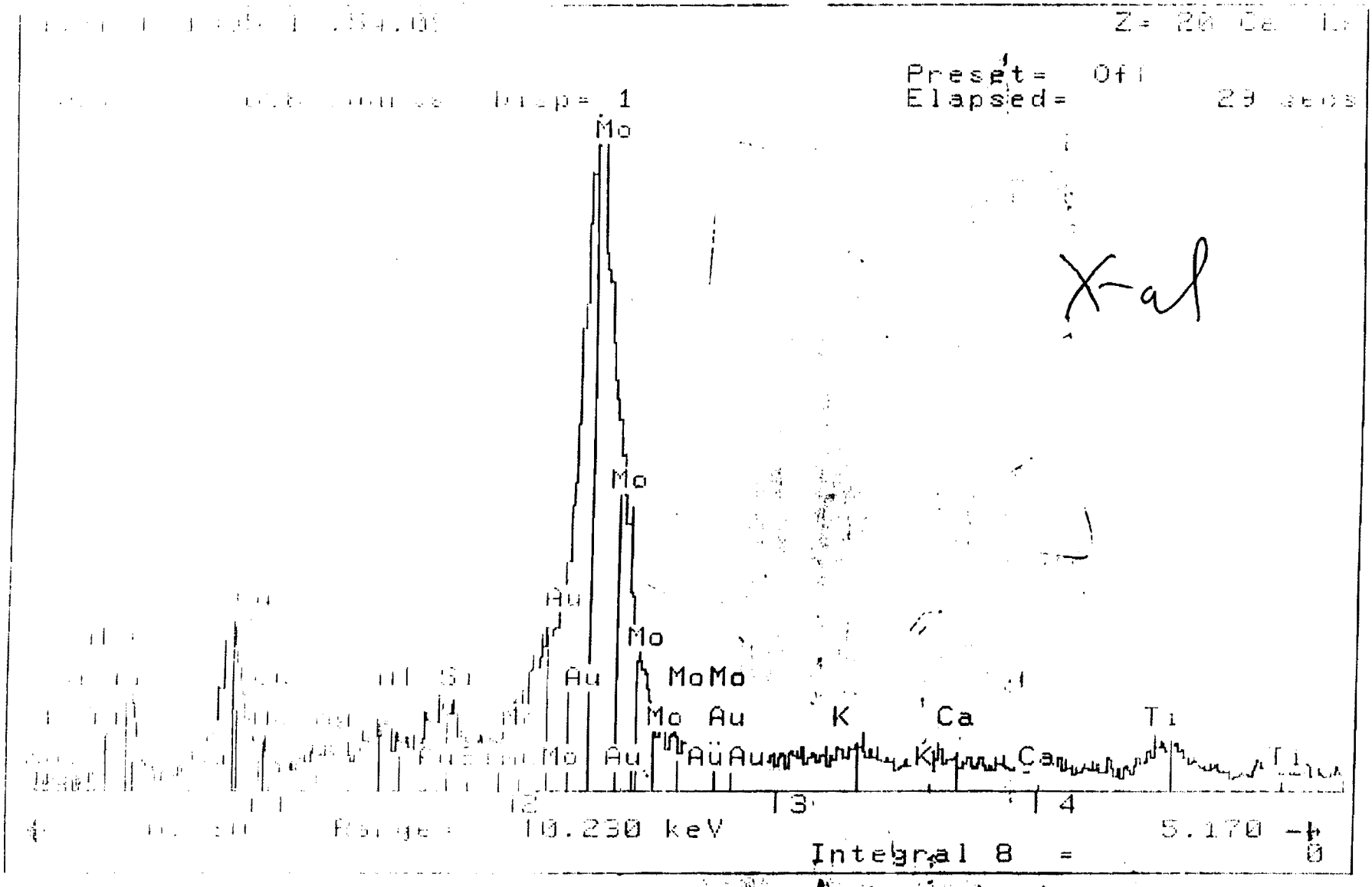
I. Introduction

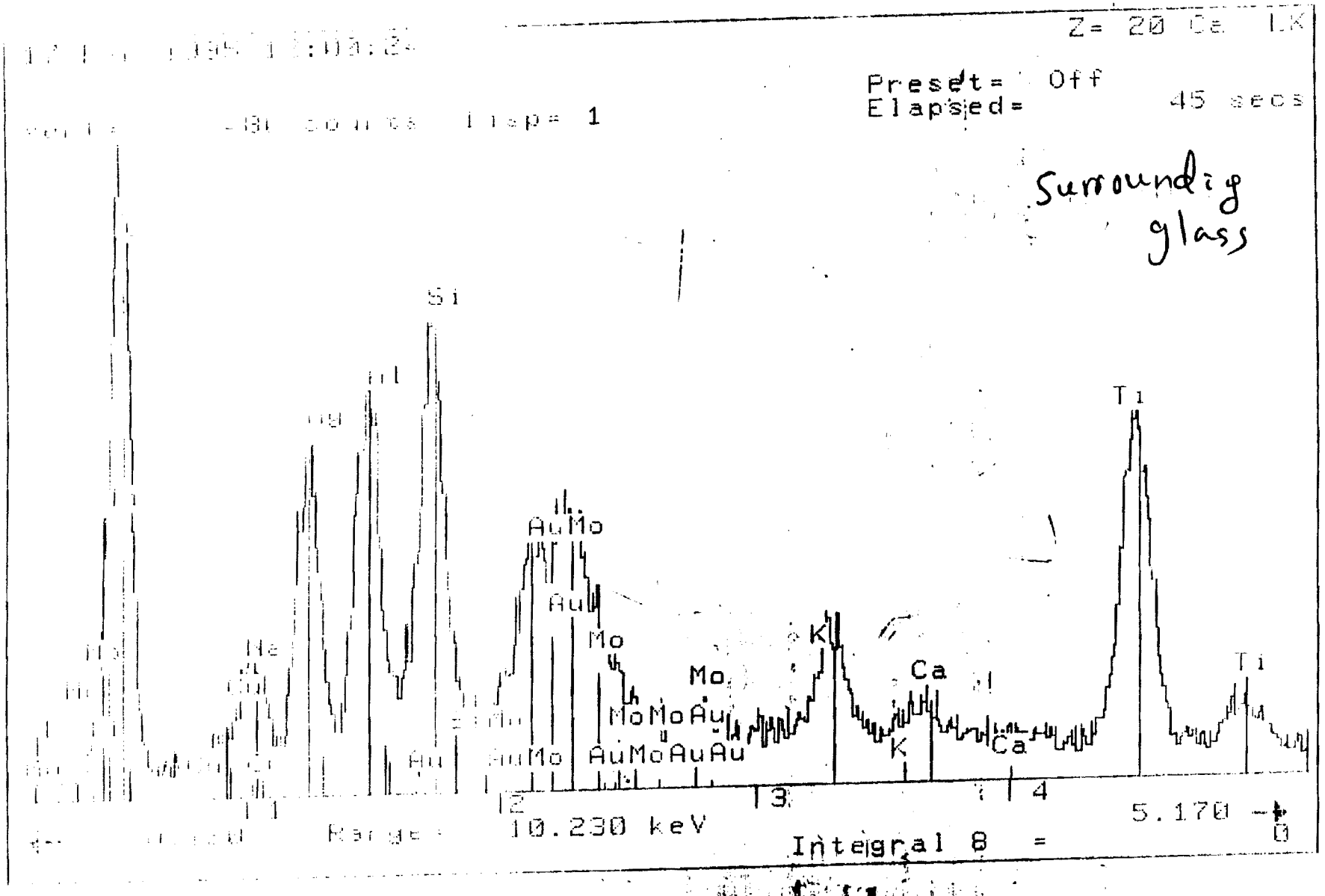
The first trial of TiB_2 application as electrode ended up with a failure. The surface of the TiB_2 electrode piece was contaminated not only by the chryolite melt but also by the unidentified materials (yellow colored). The surface of TiB_2 needs to be characterized.

II. Results

As shown in the attached EDS spectra, evidemces of molybdenum crystal, sodium-magnesium aluminosilicate glass, and pottasium and molybdenum oxides were identified. Molybdenum should be avoided as glue material.


GLASS


Preset= Off
Elapsed= 29
Mo
Mo
Au
Mo
Au
MoMo
Mo Au K Ca Ti
Mo Au Au K Ca Ti
3
4
10.230 keV
5.170
Integral 8 =
0


Z= 20 Ca
Preset= Off
Elapsed= 45 secs
Surrounding glass
Si
Au
Mo
Mo
Au
Mo
Mo
Mo
Au
Au
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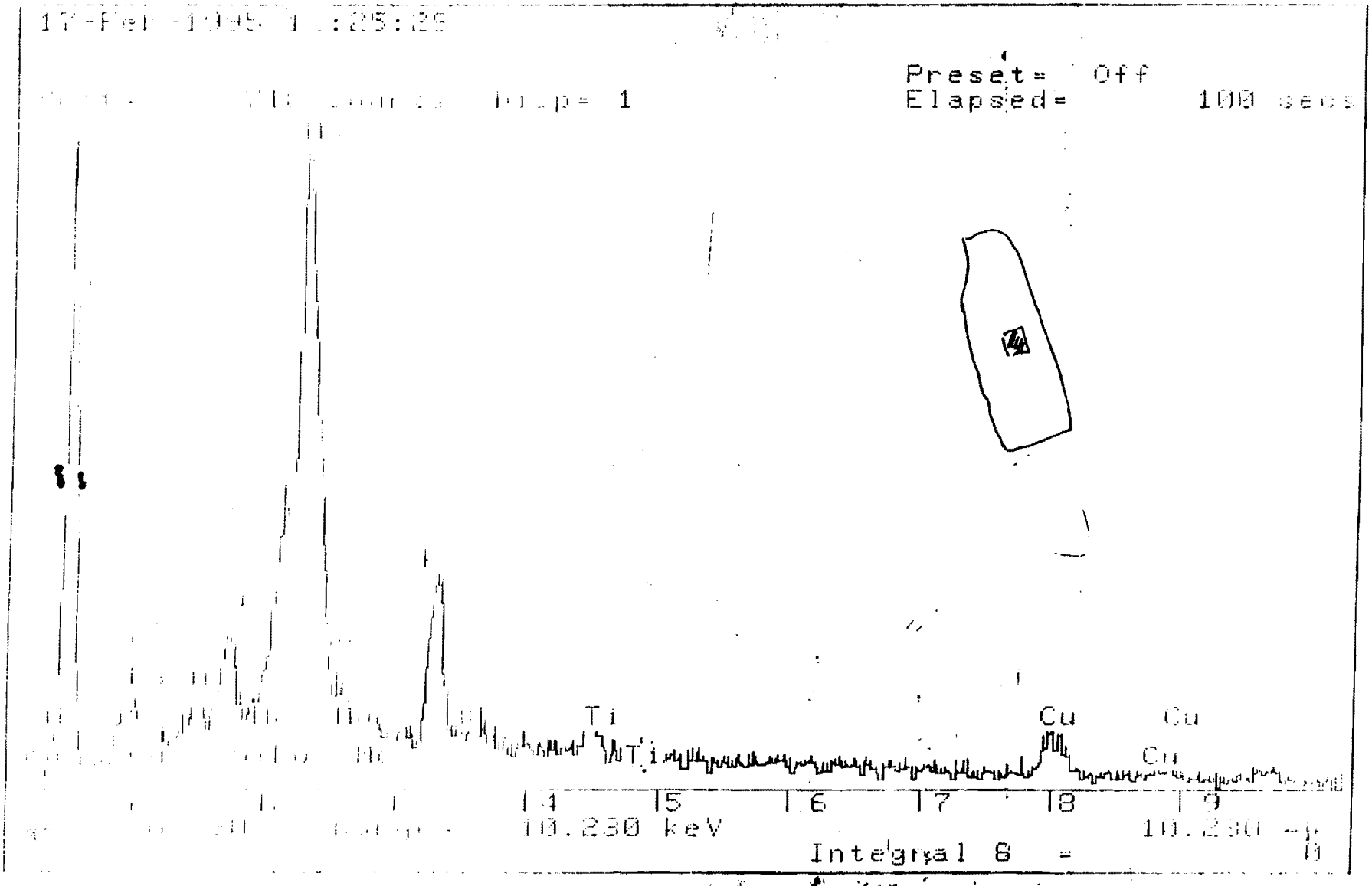
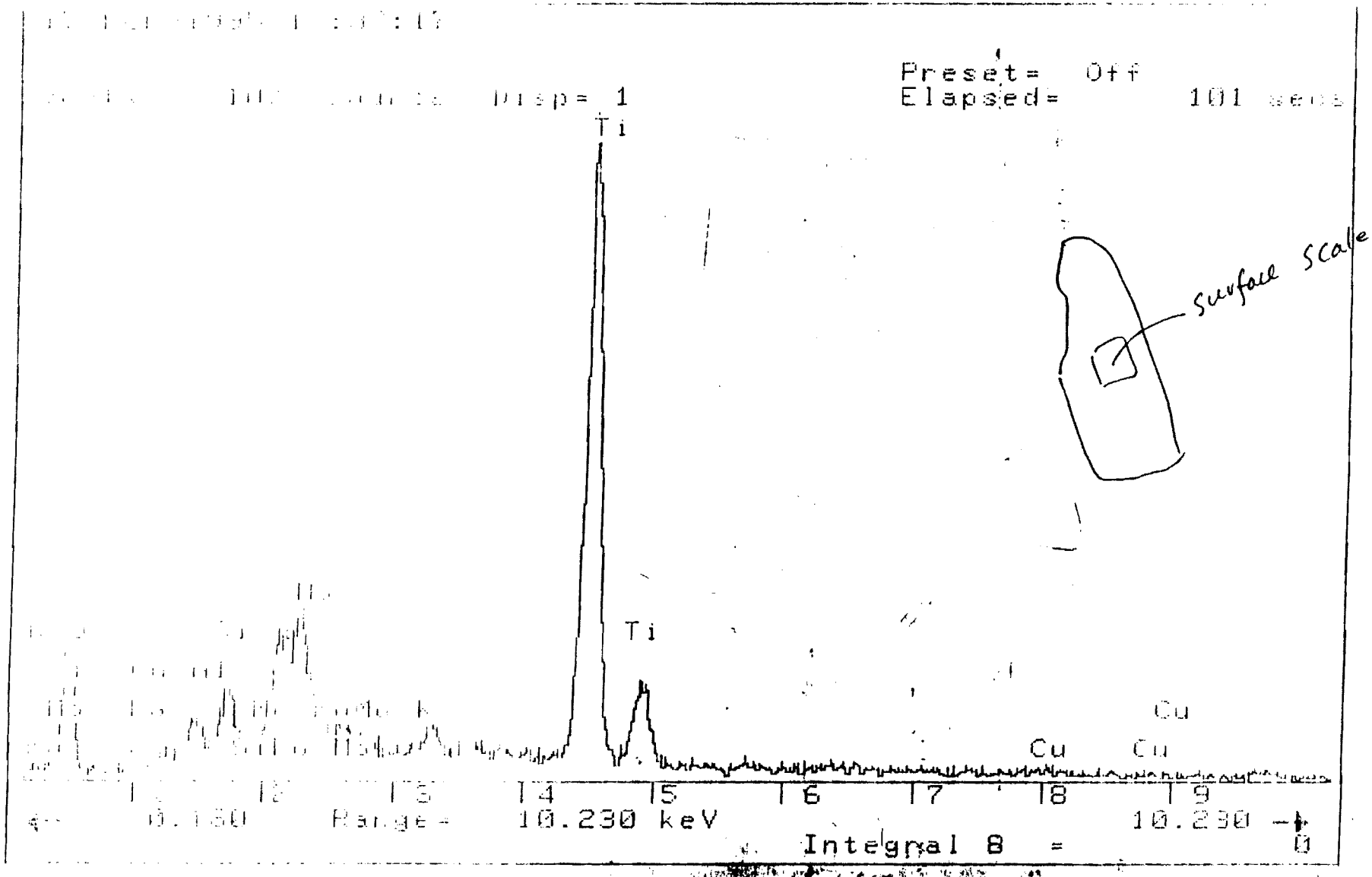
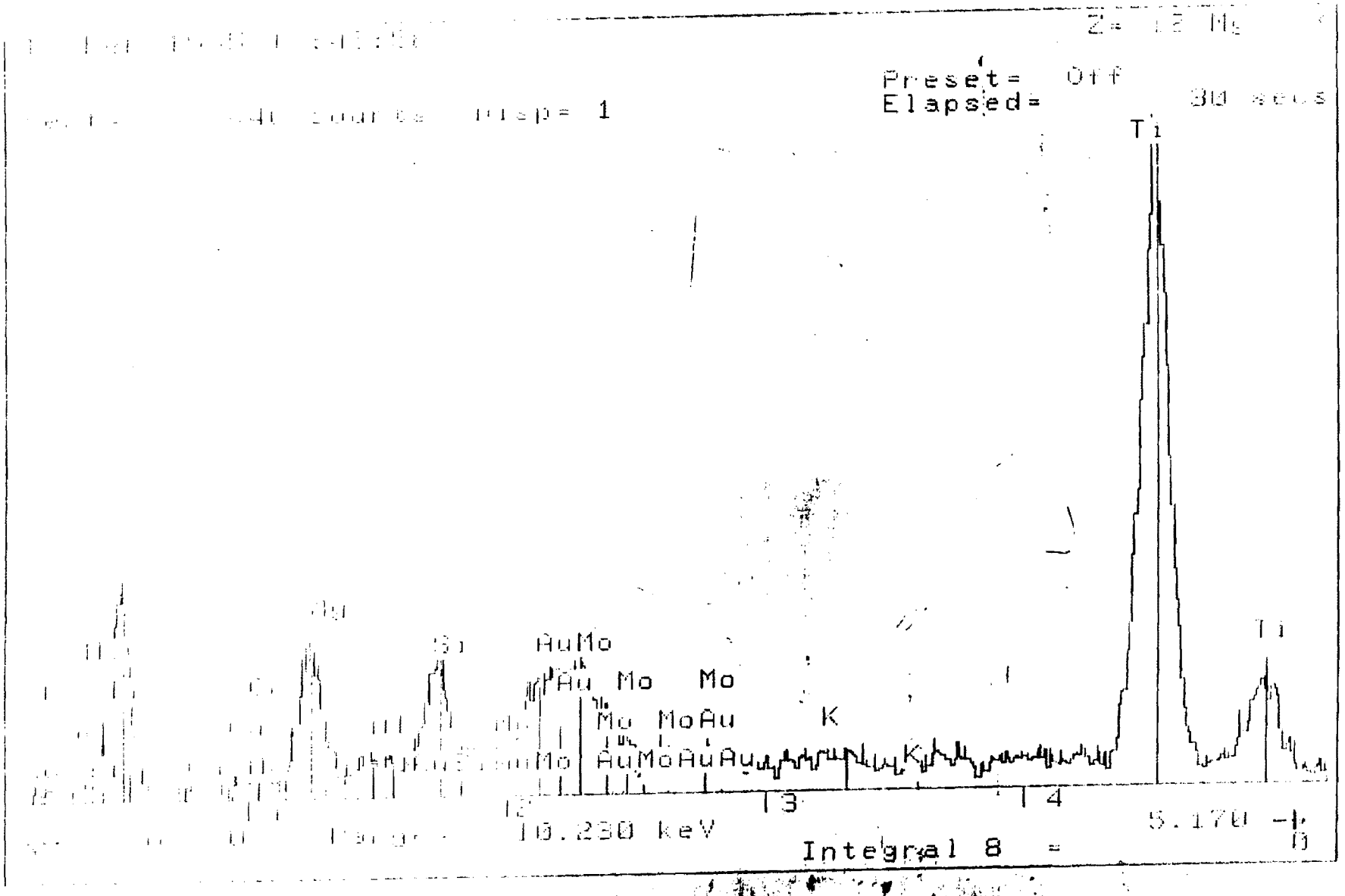
3
4
10.230 keV
5.170
Integral B =


Preset= Off
Elapsed=
Ti
Ti
Cu
Cu
Cu
4
5
6
7
8
9
10.230 keV
10.230
Integral 8 =


Preset= Off
Elapsed= 101
Disp= 1
Ti
Ti
Cu
Cu
Cu
surface scale
1 2 3 4 5 6 7 8 9
0.150 Range= 10.230 keV 10.230
Integral 8 = 0


Preset= Off
Elapsed=
Ti
Ti
AuMo
Au Mo Mo
Mo MoAu K
Mo AuMoAuAu K
2
3
4
10.230 keV
5.170
Integral 8 =

File:disk#1.aem

Characterization of TiB_2 Disk #1

Hyunho Shin

School of Materials Science and Engineering,

Georgia Institute of Technology, Atlanta, GA 30332.

I Introduction

The microstructure of TiB_2 disk produced by magnesium thermite reaction, followed by hot pressing at 1580°C, was characterized. The polished surface of the disk was like a mirror. The mirror planed surface was investegated using SEM/EDS without coating.

II Results and Discussion

Figure 1 shows that the TiB_2 grains grow in the faceted rectangular frorm. The growth of the hard TiB_2 in such a form results in a void in triangular and rectangular forms. These voids are interpreted to be filled with a relatively soft oxide phase, which are squeezed out from TiB_2 grain growth area. The dark phase in the figure are shown to be rich in magnesium as shown in the following EDS spectra for Figure 2.

Figure 2 shows four distinct areas in the TiB_2 microstructure — dark area, white area, faceted crystal, and lamellar bright area adjacent to the faceted crystal. The lamellar bright area is shown in detail in Figure 3. The dark area is rich in magnesium, oxygen, and titanium

as shown in the attached spectra, interpreted to be magnesium titanium oxide glass phase. Such a glass phase would flow to fill up the angled voids after squeezed out from the hard TiB_2 growth area. This indicates that the leaching process was not complete and hence the residual MgO liquid phase helped densification at lowered hot pressing temperature. Literature survey indicates that pure TiB_2 densified at 1900°C for 60 min resulted in a 70% dense sample! However, the disk sample was more than 90% dense while it was hot pressed at an obviously lower temperature. Hence, the residual MgO phase due to the incomplete leaching is speculated to form a liquid phase and then fostered the densification of the hard TiB_2 grains.

The growth of TiB_2 crystals as a faceted retangular form and angled voids associated with them indicates that merely a longer hot pressing period does not improve the densification much. A rapid heating rate with a maximal pressure at an early hot pressing stage would help densification. In other words, there should not be a chance for the TiB_2 grains grow too much. As far as the faceted TiB_2 grains fracture in unision with other matrix phases, the aspect (length to equivalent diameter) ratio of such TiB_2 grains would not result in any appreciable difference in fracture toughness. Hence we don't have to worry about loosing the aspect ratio of the grains by not allowing them to grow much.

As a quick method, we can simply measure the Vicker's hardness value of the as-pressed and polished specimen in order to compare with the reported pure TiB_2 values. This would easily give the degree of oxide phase presence in the sample. A very nice Vicker's hardness indenter is available in Dr. Cochran's area.

The EDS results from the white areas marked as γ and ϵ in sketches of Figure 2 show

somewhat unexpected elements — apparent detection of Fe and P indicates an apparent sample contamination during processing.

Figure 3a shows a more detailed image of the lamellar bright areas sketched in Figure 2. These areas, in general, surround the grown TiB_2 grains. However they are observed independently very often as shown in Figures 3a and 3b. In Figure 3b, these areas formed an independent grain structure — indeed, they have an unusual circular structure in the lamellar shaped TiB_2 majority. Those circular areas and the lamellar structures adjacent to the TiB_2 grains were rich in titanium ans nitrogen as shown in the attached EDS spectra. In order to confirm the presence of TiN phase, a TEM investigation of such an area is required.

Figure 1

Figure 2


000101 15KV X6.0K 6.0um

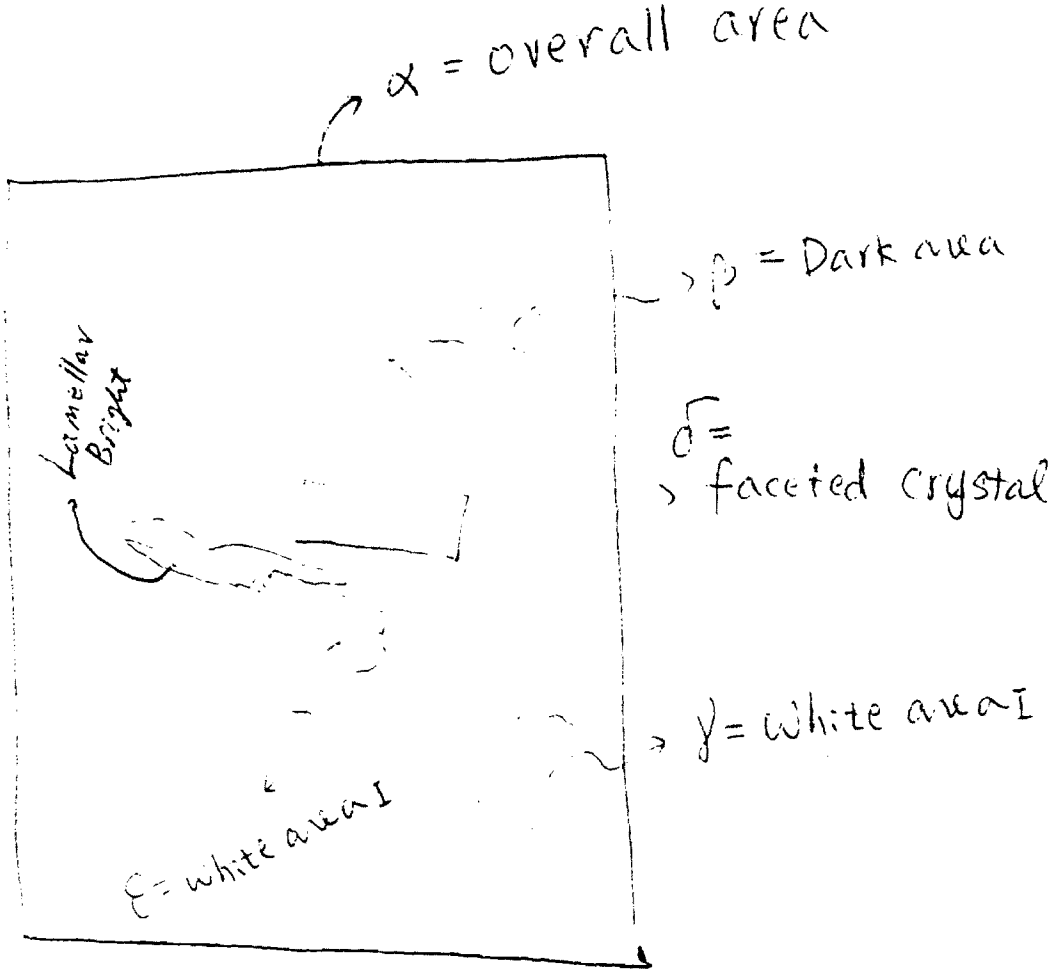
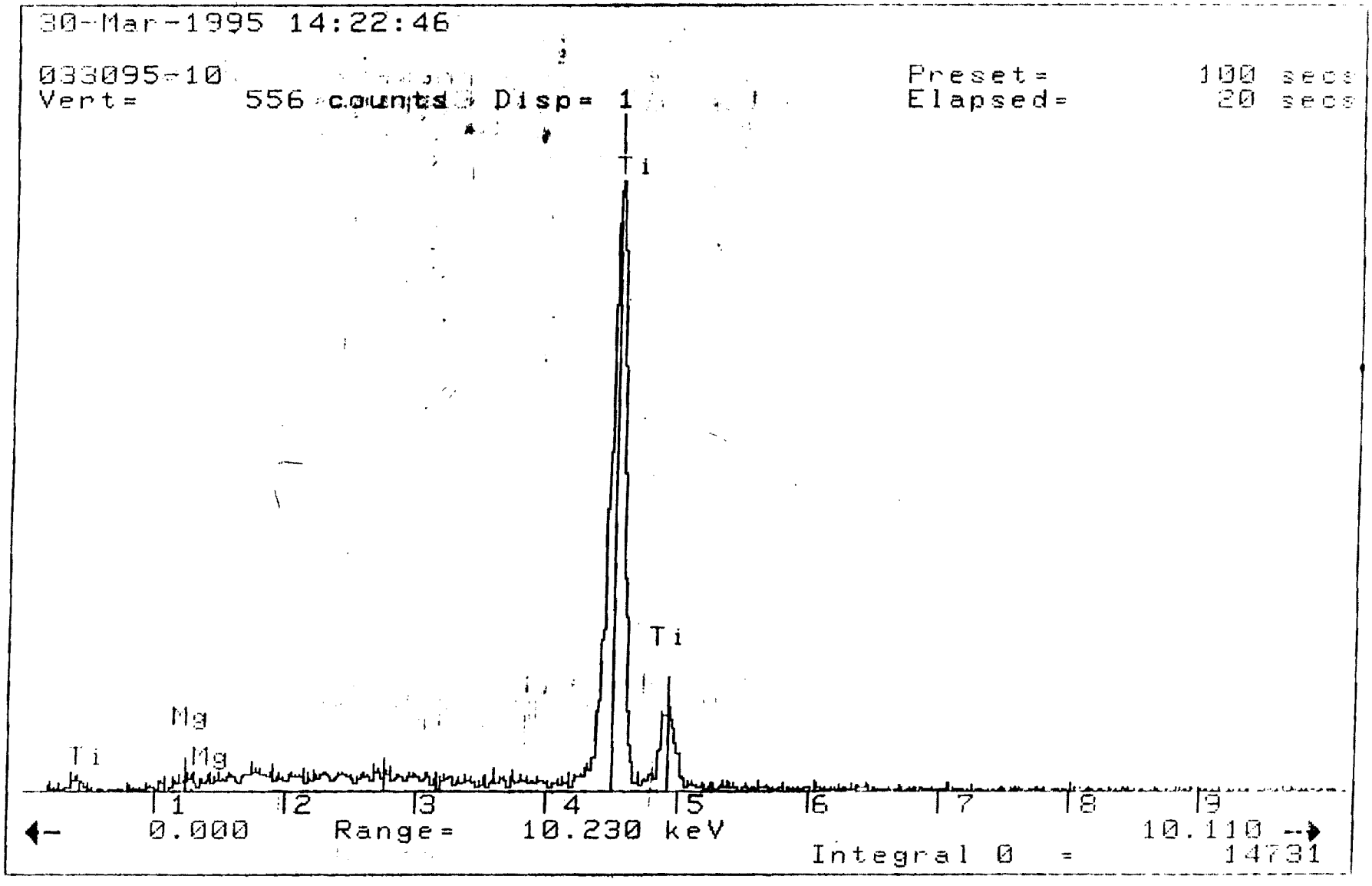

α = overall area
β = Dark area
δ = faceted crystal
γ = white area I
ε = white area I
Lamellar Bright

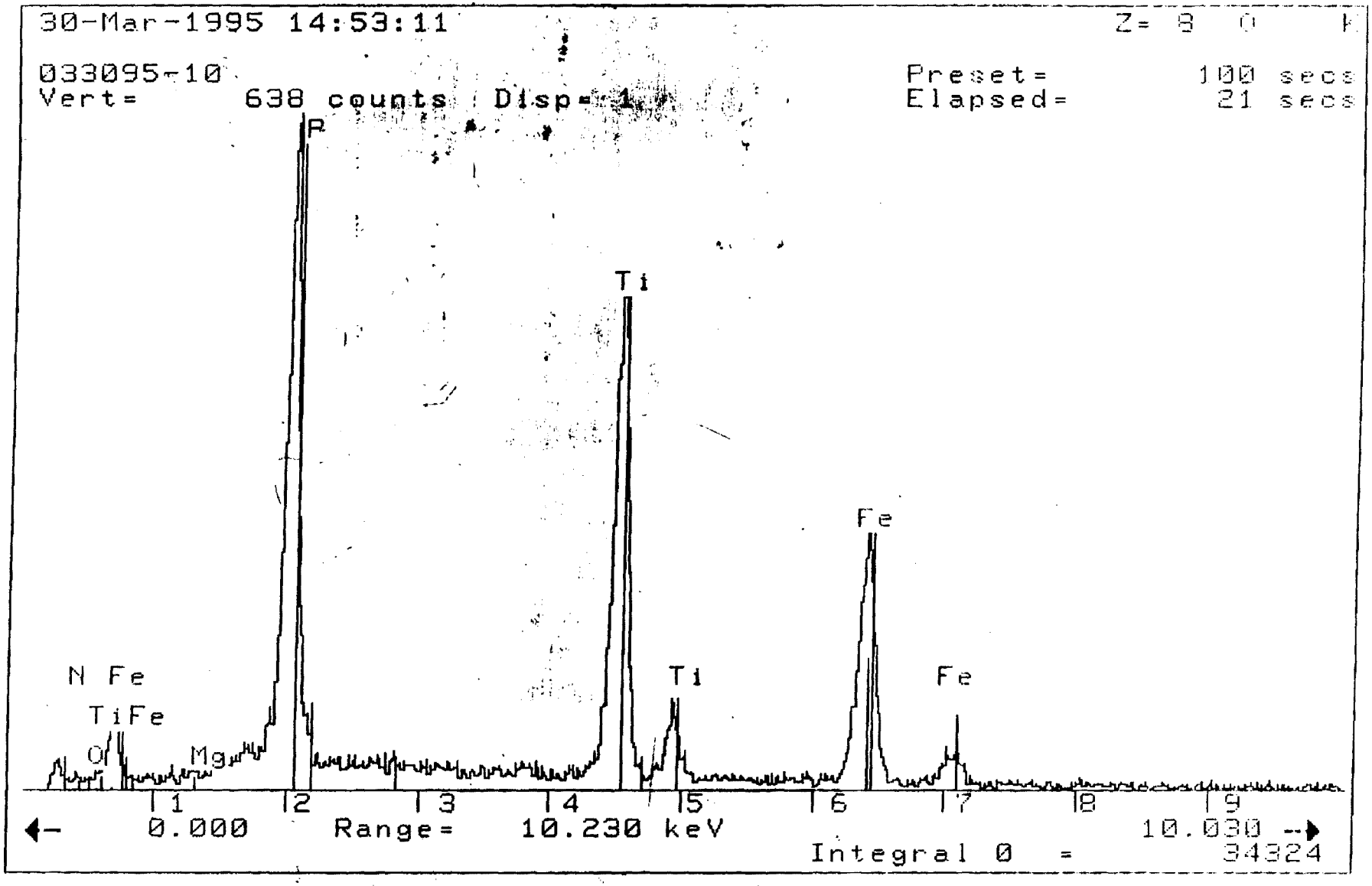
Figure 3

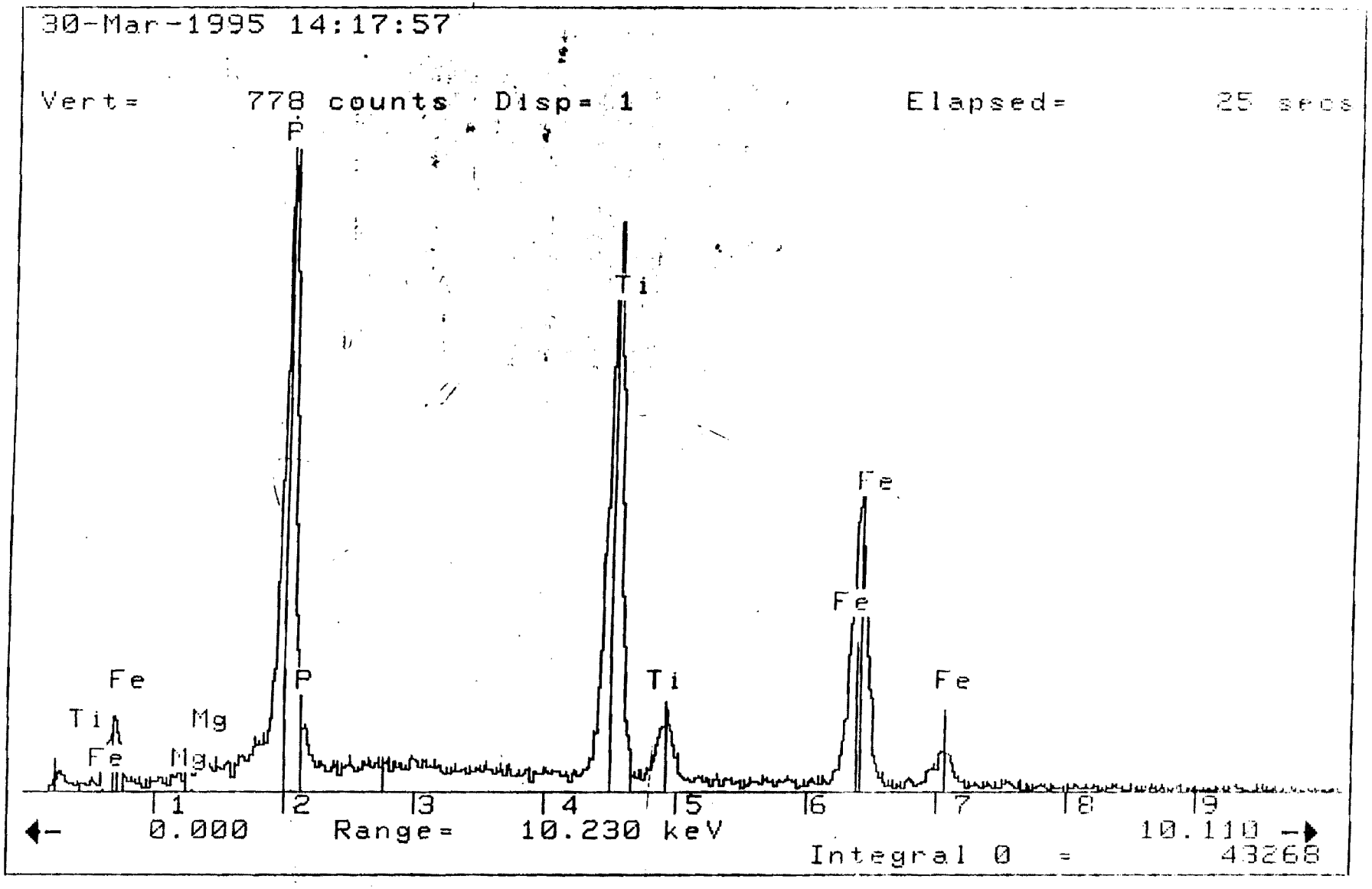
(a)

(b)

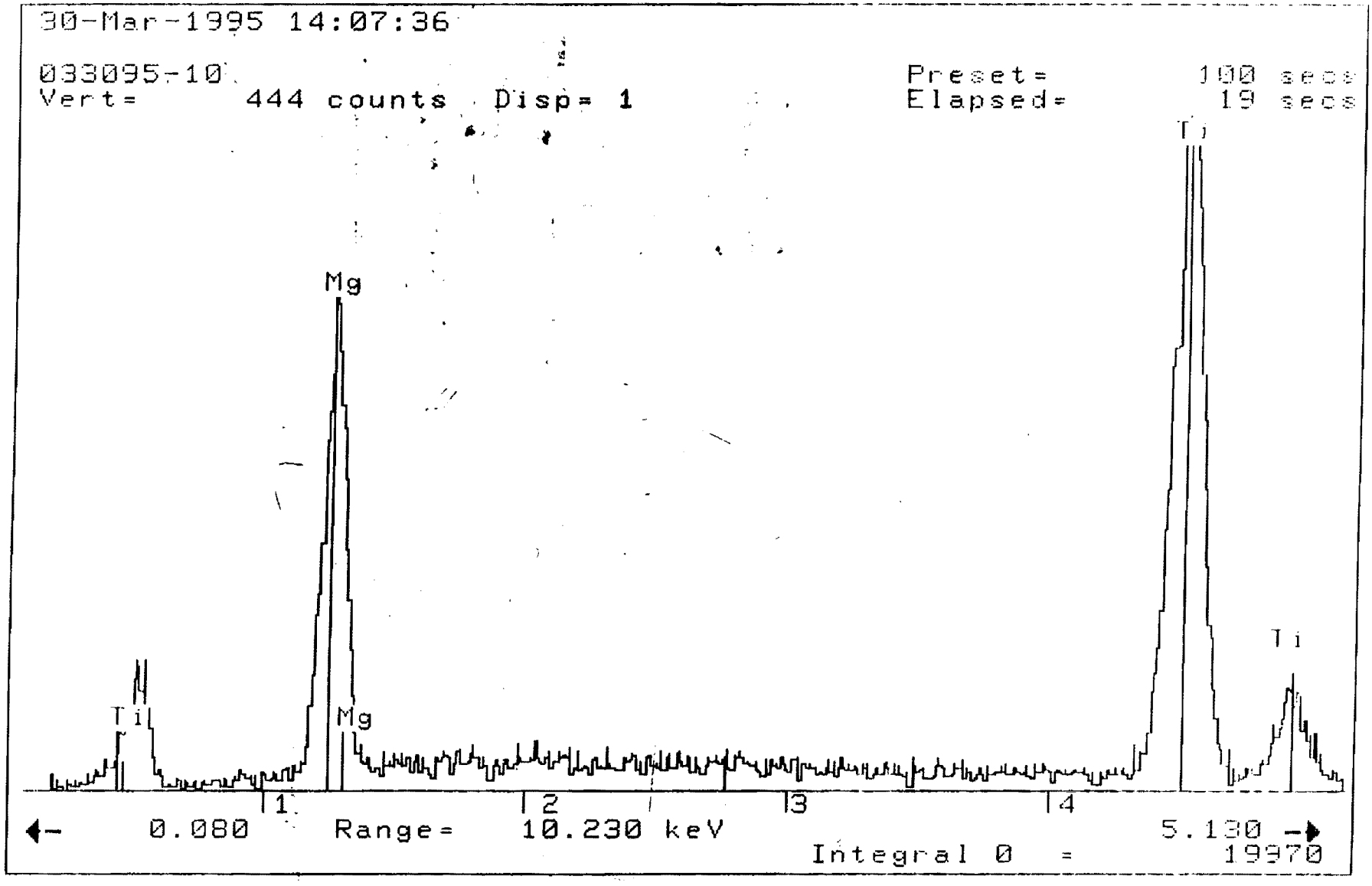

30-Mar-1995 14:22:46
033095-10
Vert= 556 counts Disp= 1
Preset= 100 secs
Elapsed= 20 secs
Ti
Ti
Mg
Ti
Mg
1
2
3
4
5
6
7
8
9
0.000
Range= 10.230 keV
10.110
Integral 0 = 14731

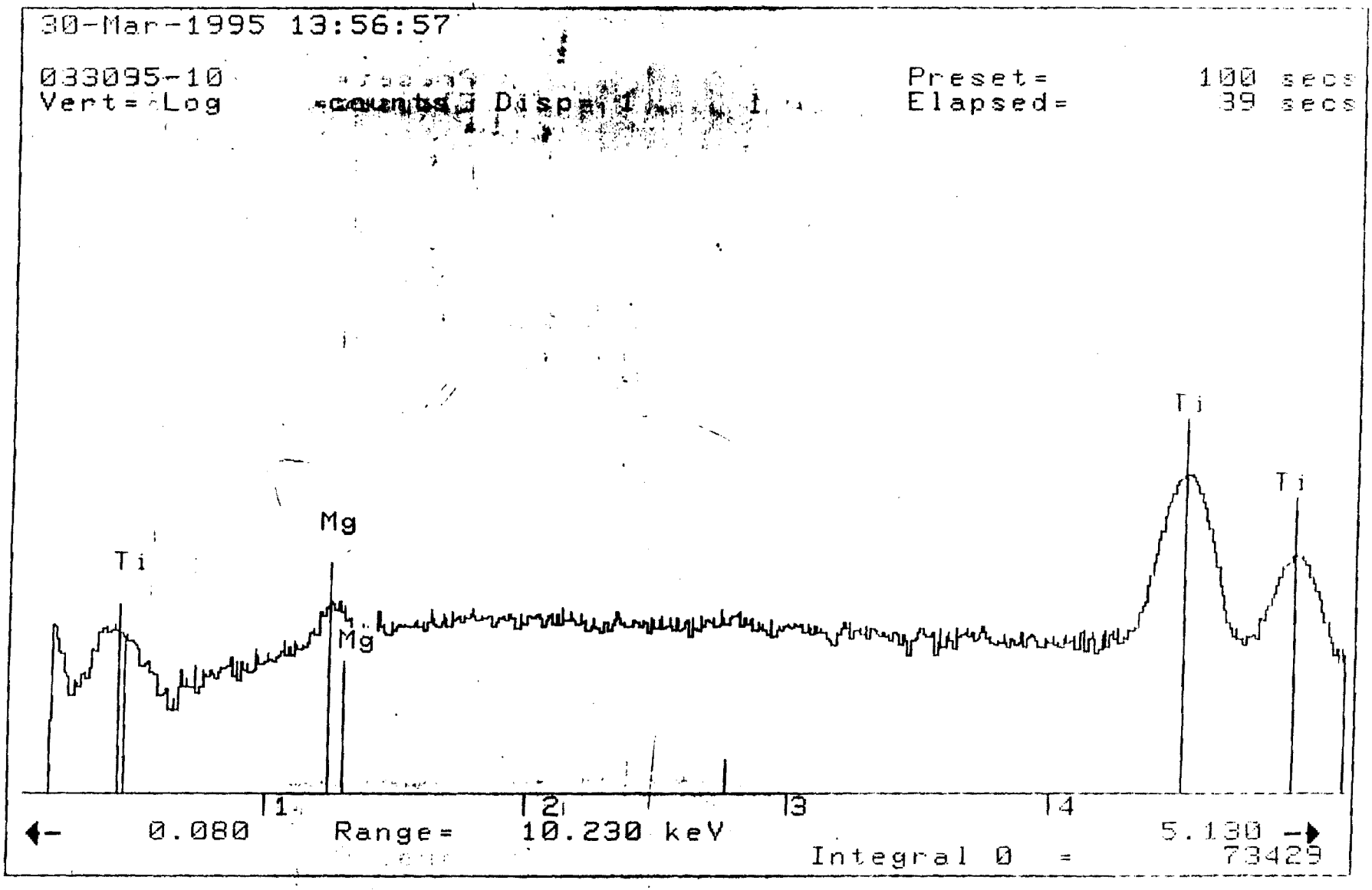
E = White area.


30-Mar-1995 14:53:11
Z= 8 O K
033095-10
Vert= 638 counts Disp= 1
Preset= 100 secs
Elapsed= 21 secs
R
Ti
Fe
N Fe
TiFe
O
Mg
Ti
Fe
1
2
3
4
5
6
7
8
9
0.000
Range= 10.230 keV
10.030
Integral 0 = 34324

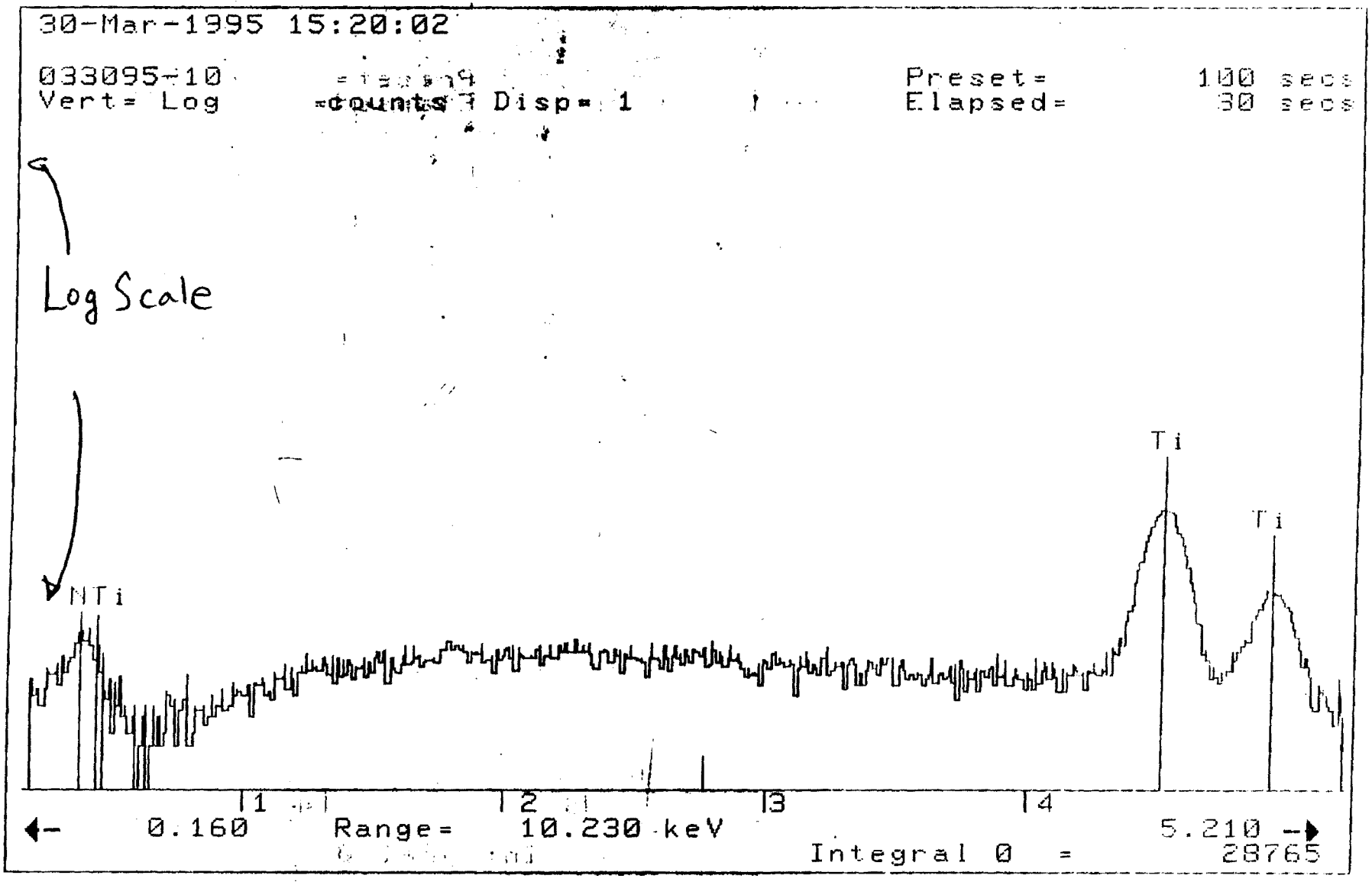

30-Mar-1995 14:17:57
Vert= 778 counts Disp= 1
Elapsed= 25 secs
P
Ti
Fe
Fe
Fe
P
Ti
Fe
Ti
Mg
Fe
Mg
1
2
3
4
5
6
7
8
9
0.000
Range= 10.230 keV
10.110
Integral 0 = 43268

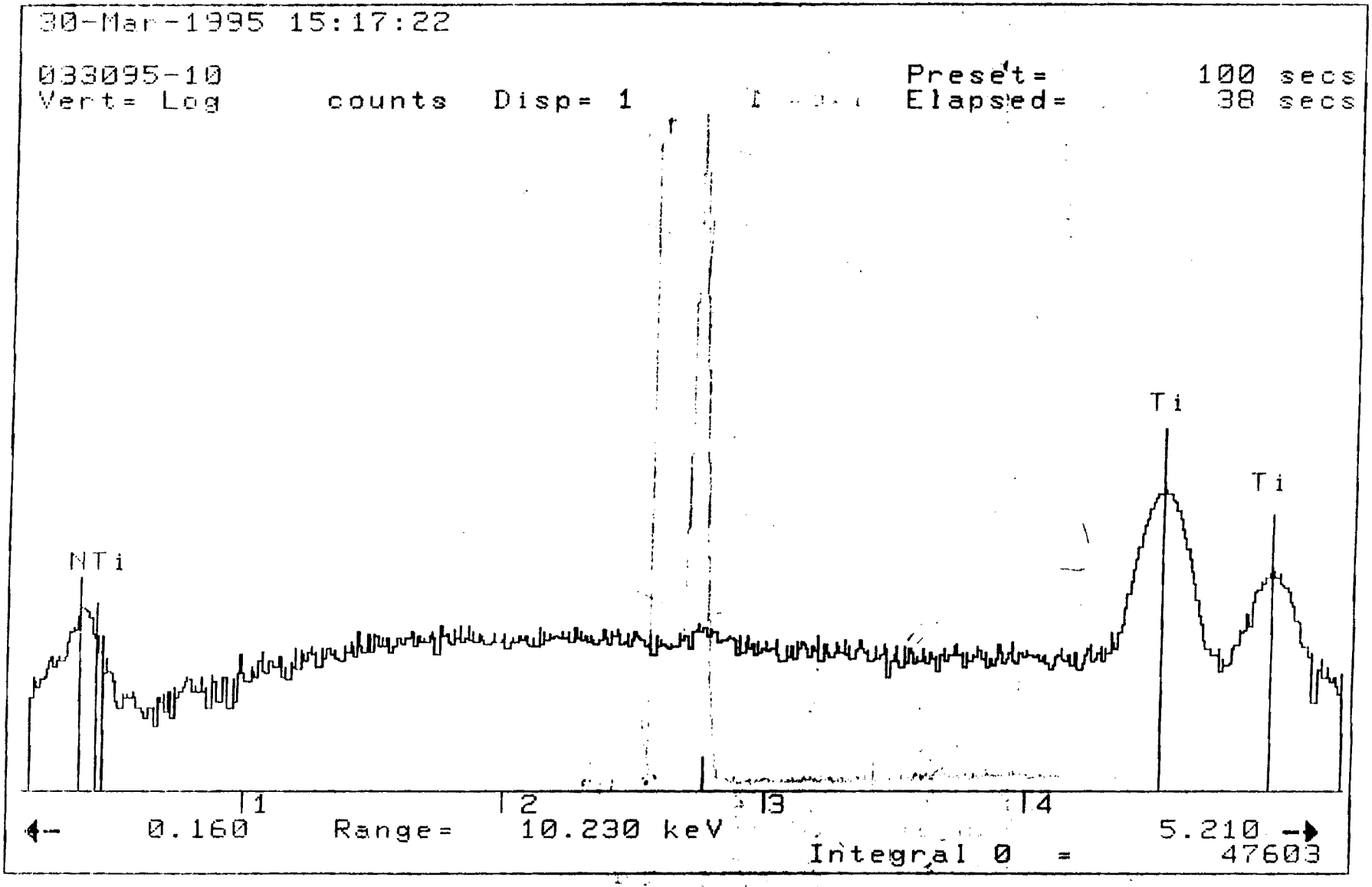
β = Barker Arc

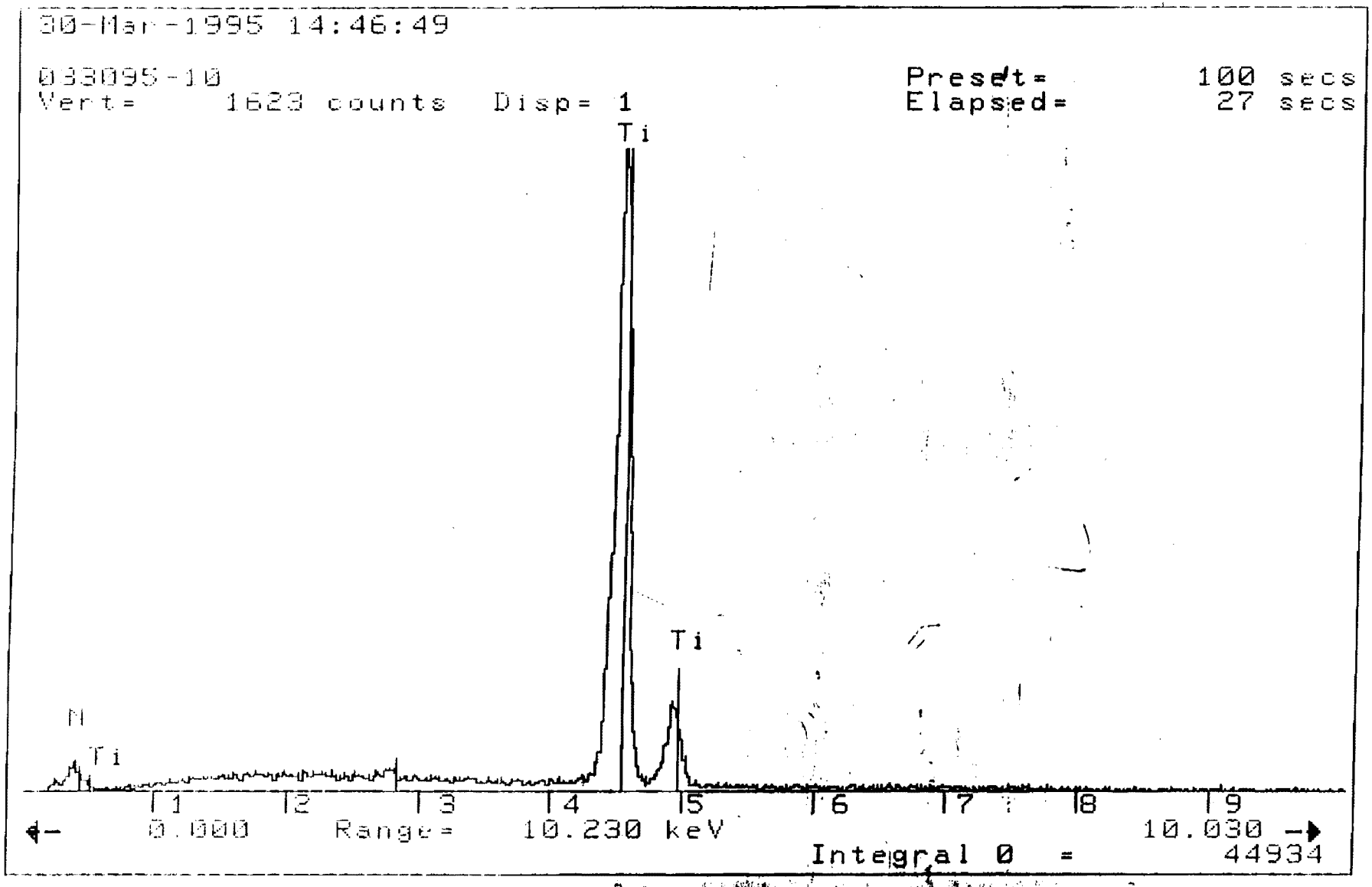

30-Mar-1995 14:07:36
033095-10
Vert= 444 counts Disp= 1
Preset= 100 secs
Elapsed= 19 secs
Ti
Mg
Ti
Mg
Ti
1
2
3
4
0.080
Range= 10.230 keV
5.130
Integral 0 = 19970

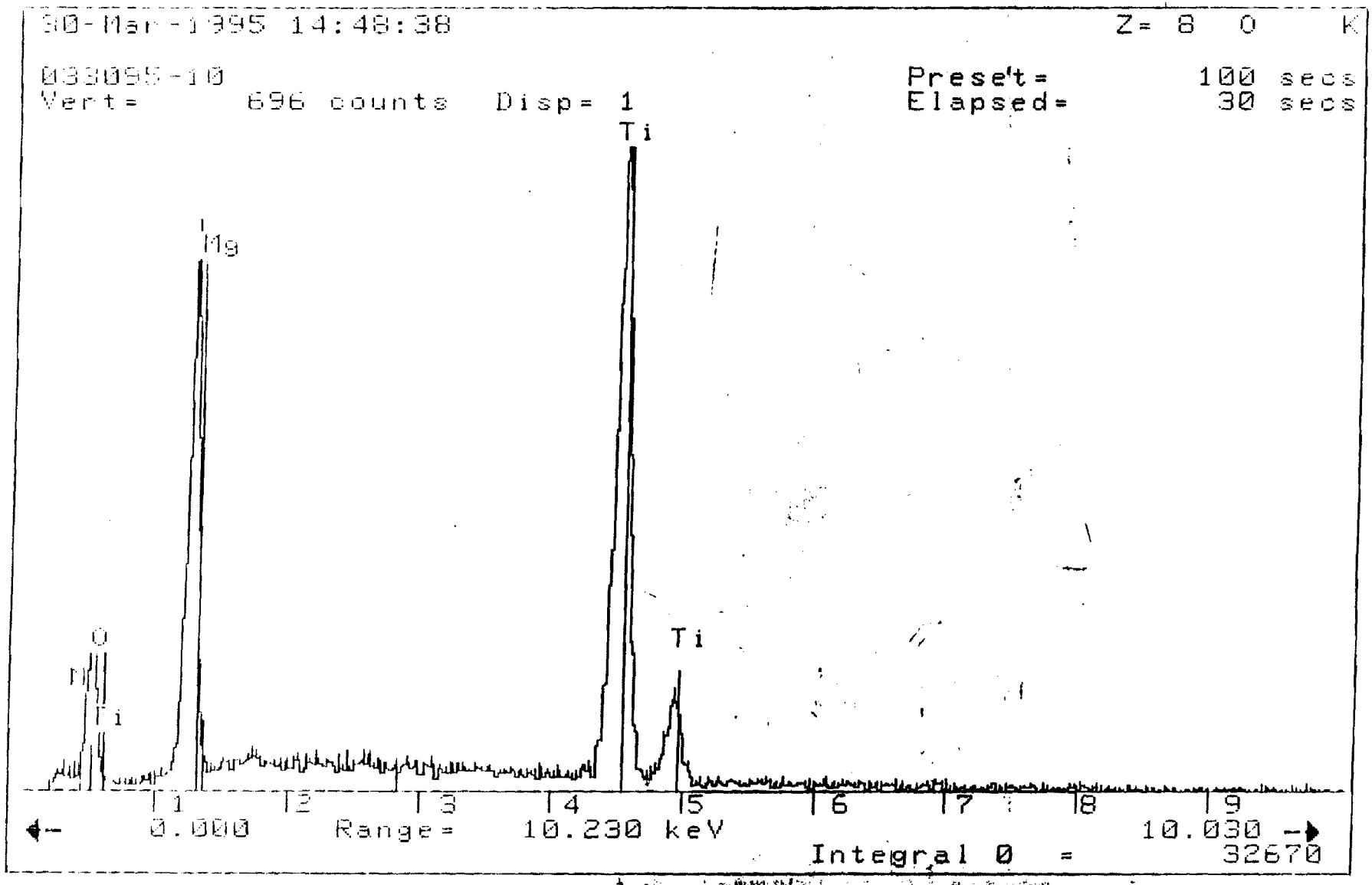

30-Mar-1995 13:56:57
033095-10
Vert = Log
Preset= 100 secs
Elapsed= 39 secs
Ti
Mg
Mg
Ti
Ti
1
2
3
4
0.080
Range= 10.230 keV
5.130
Integral 0 = 73429

Lamellar right




30-Mar-1995 15:17:22
033095-10
Vert= Log
counts
Disp= 1
Preset= 100 secs
Elapsed= 38 secs
NTi
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 47603


30-Mar-1995 14:46:49
033095-10
Vert= 1623 counts Disp= 1
Preset= 100 secs
Elapsed= 27 secs
Ti
Ti
N
Ti
1
2
3
4
5
6
7
8
9
0.000
Range= 10.230 keV
10.030
Integral 0 = 44934


30-Mar-1995 14:48:38
Z= 8 O K
030395-10
Vert= 696 counts Disp= 1
Preset= 100 secs
Elapsed= 30 secs
Ti
Mg
O
Ti
Ti
1
2
3
4
5
6
7
8
9
0.000
Range= 10.230 keV
10.030
Integral 0 = 32670

Characterization of the Third TiB_2 Electrode after Service

By Hyunho Shin

February 17, 1995

I. Introduction

The third trial of TiB_2 application as electrode ended up with impact weakened TiB_2. The fracture surface of the TiB_2 electrode piece was intended to be characterized.

II. Results

The apparent surface scale as sketched in Figure 1, is due to the chryolite attack. As shown in the attached EDS spectra, evidences of rich Ti (area 1 - 5, 7) with F, Na, and Al (area 9) supports this. The inner portion of the sample showed black spots. This is sketched in Figure 1 and the real picture is shown in Figure 2. The detailed magnified view is shown in Figure 3. As shown in the last two spectra (written as stone and matrix area), these black stone areas are rich in Na, O, and Ti. The diffusion of sodium oxide from TiB_2 surface was apparent. The density of the TiB_2 sample should be checked.

Figure 1.

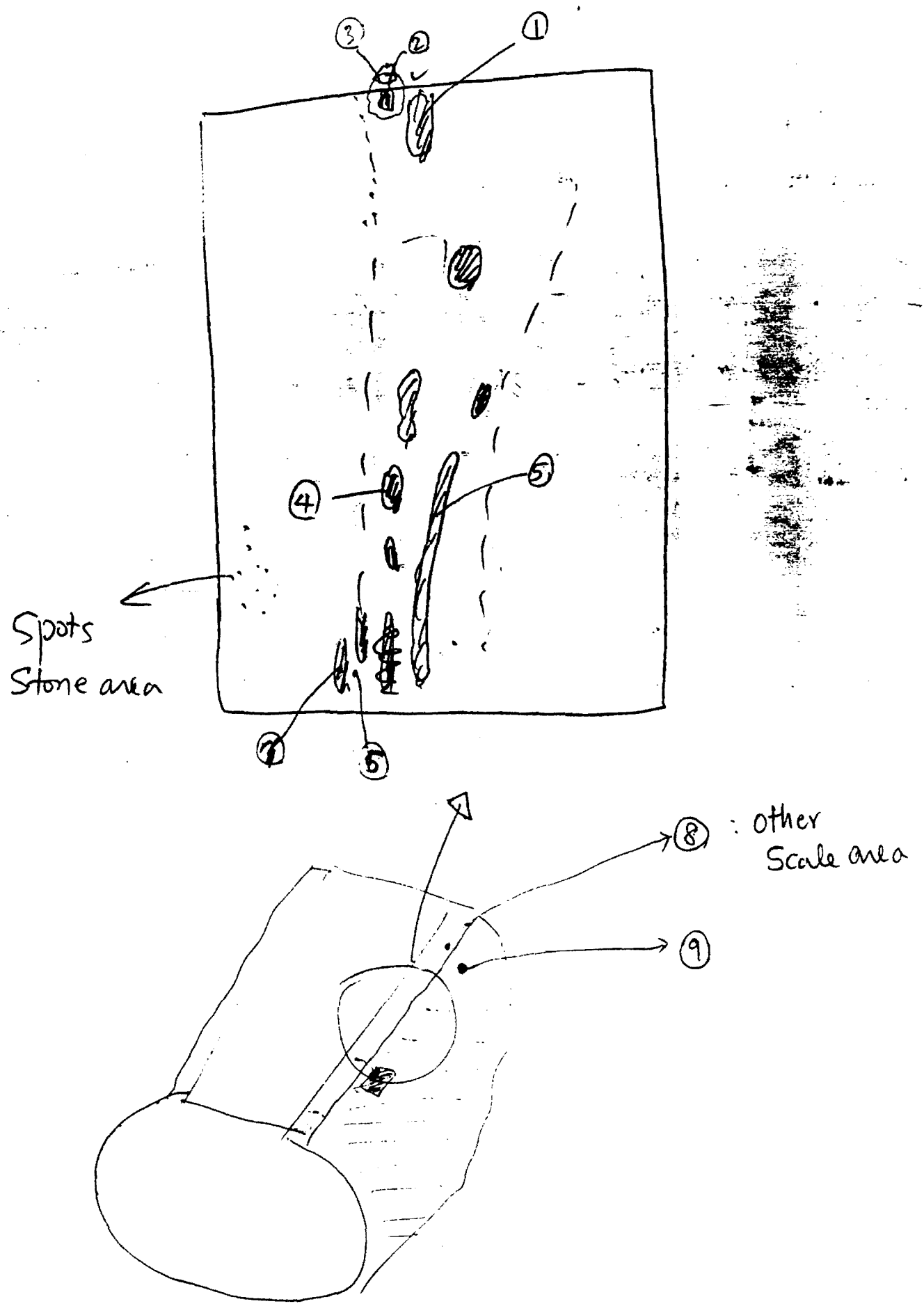
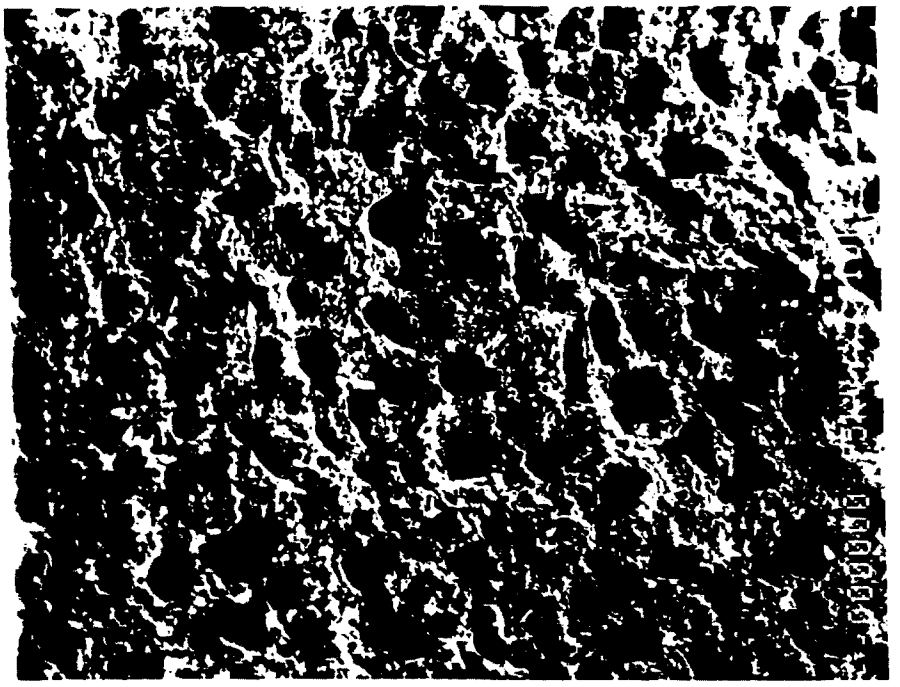


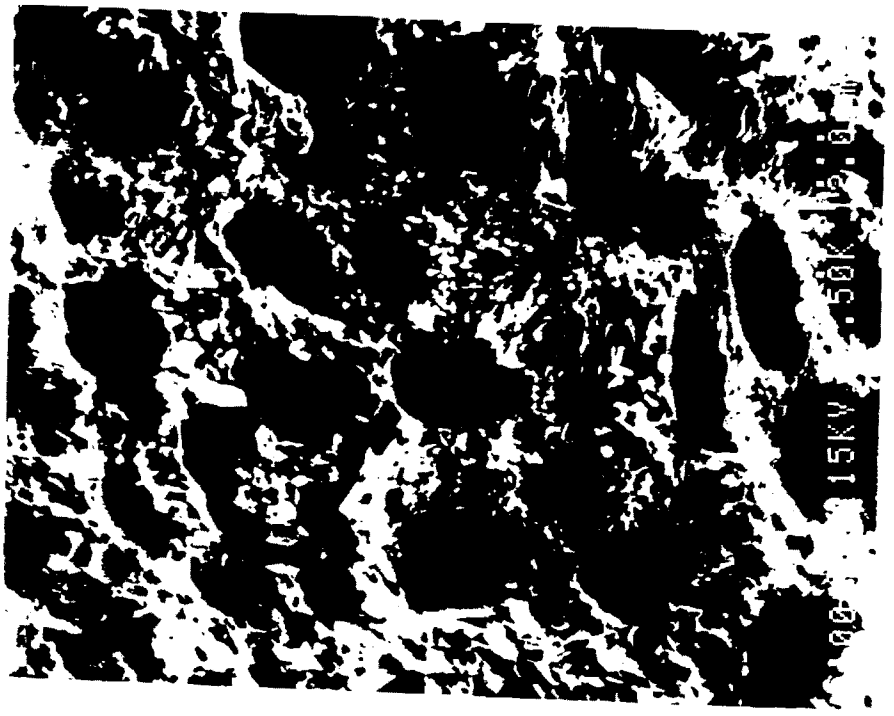
Figure 2

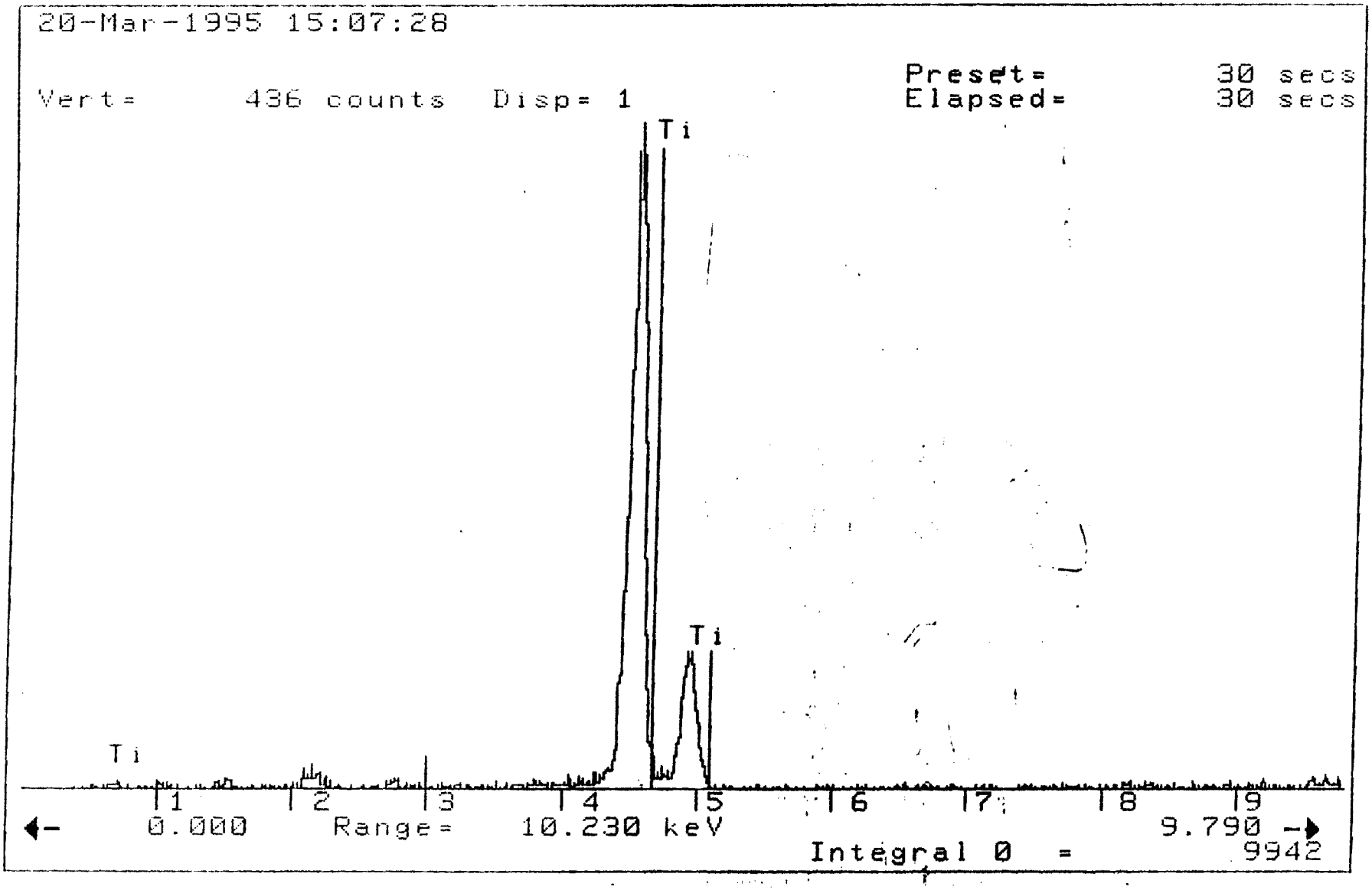
surface scale

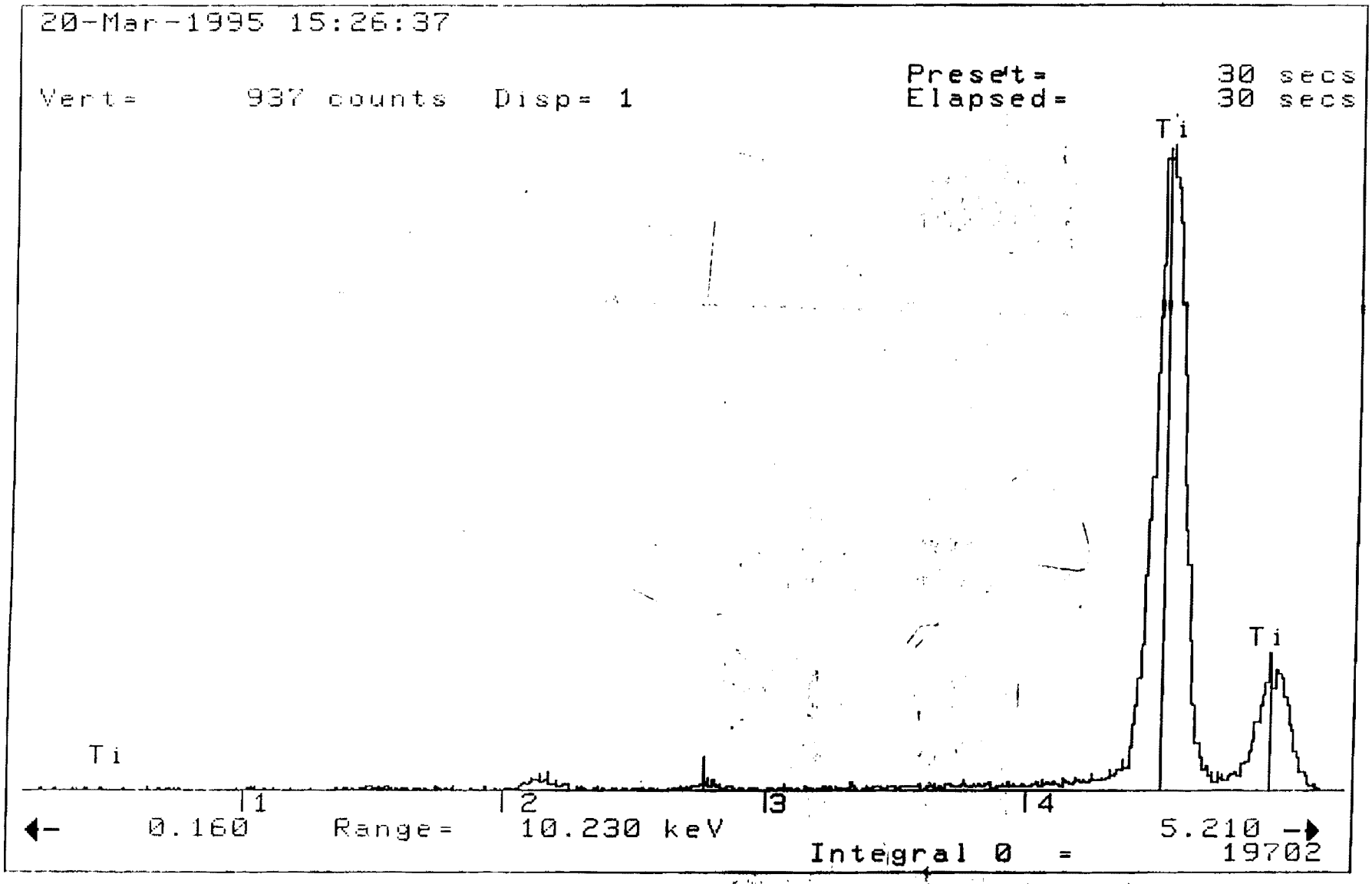
#1 ~ #7 area

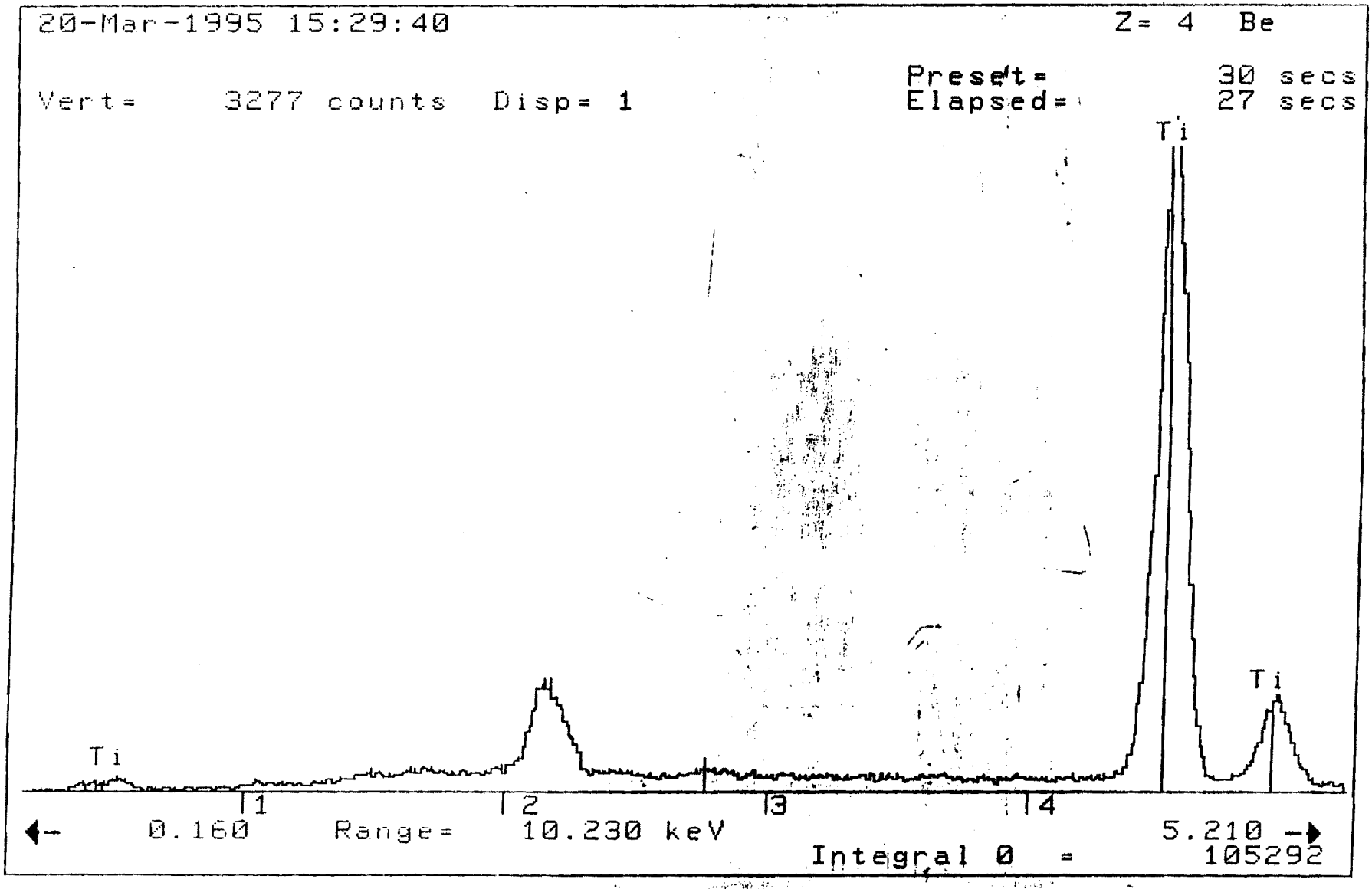
Figure 3

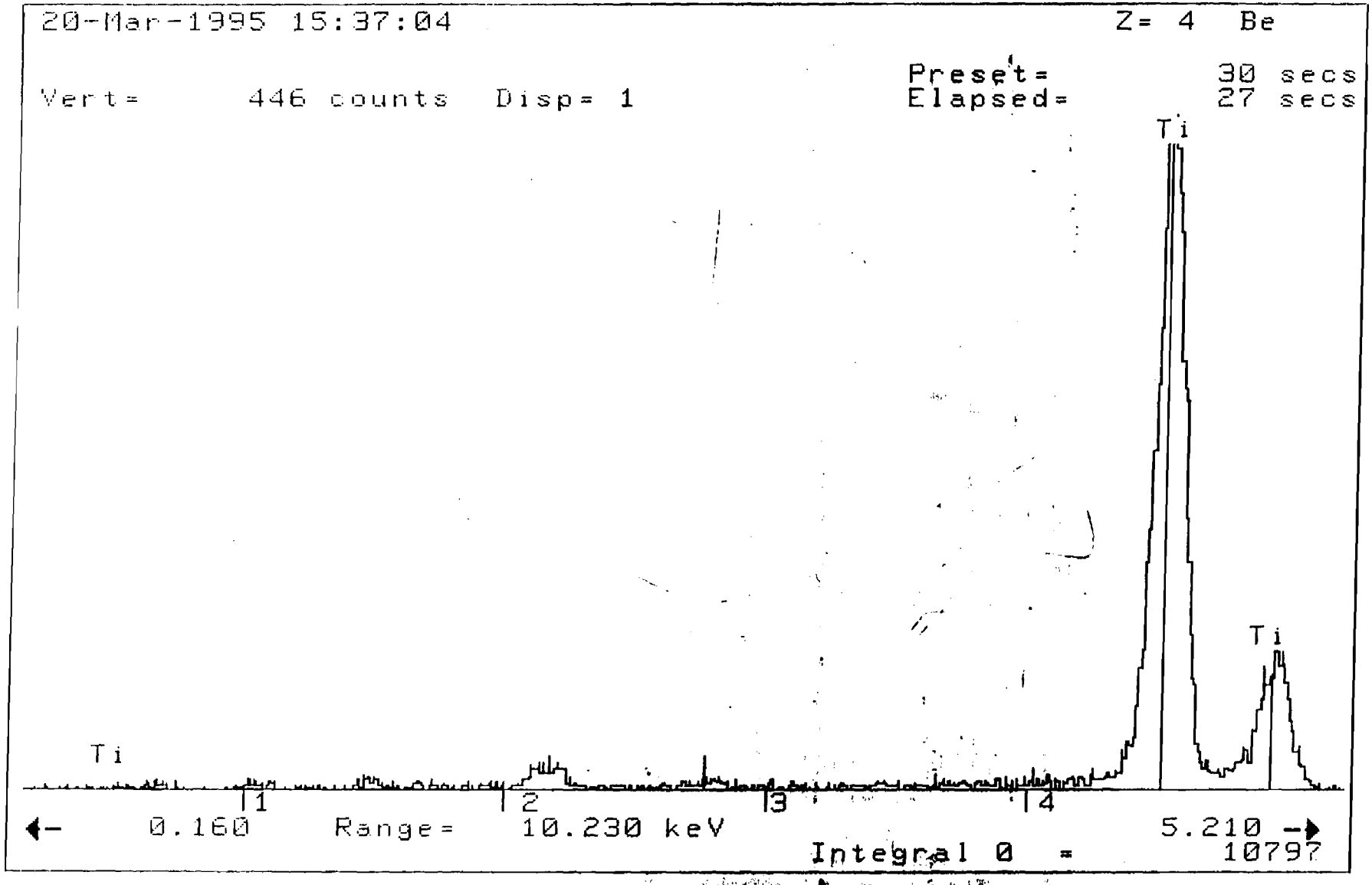


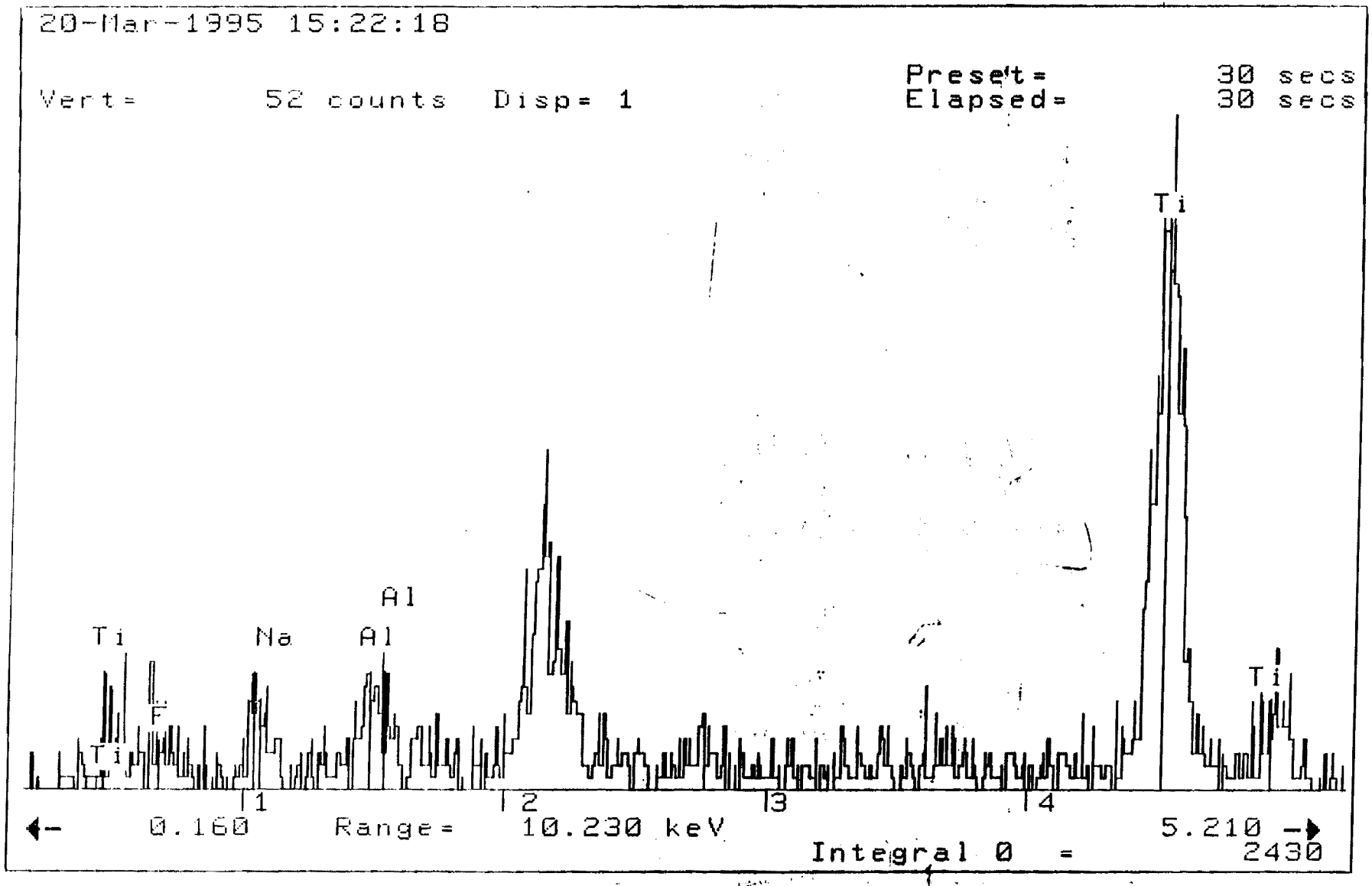


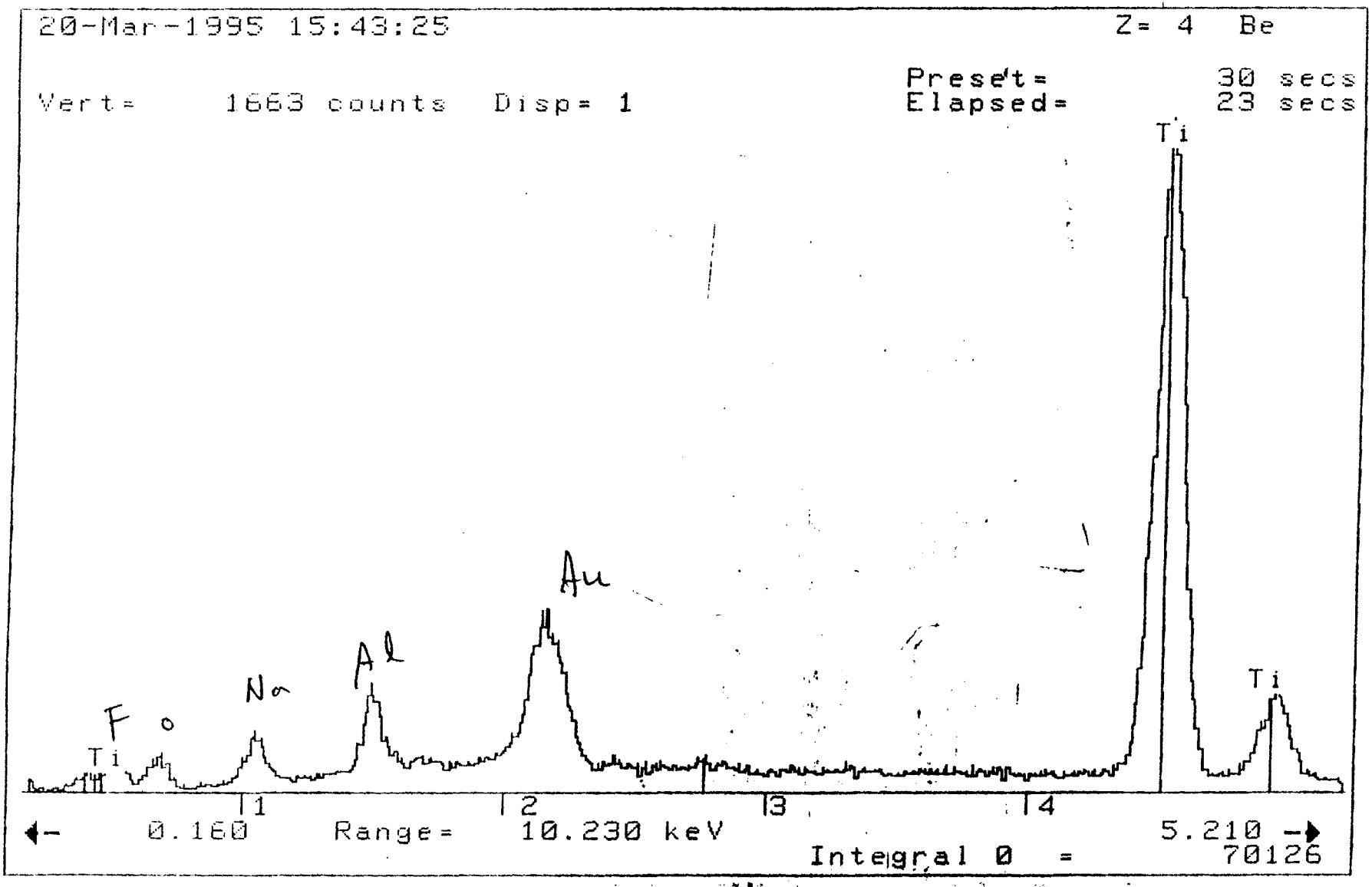

20-Mar-1995 15:07:28
Vert= 436 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
Ti
Ti
Ti
1
2
3
4
5
6
7
8
9
0.000
Range= 10.230 keV
9.790
Integral 0 = 9942

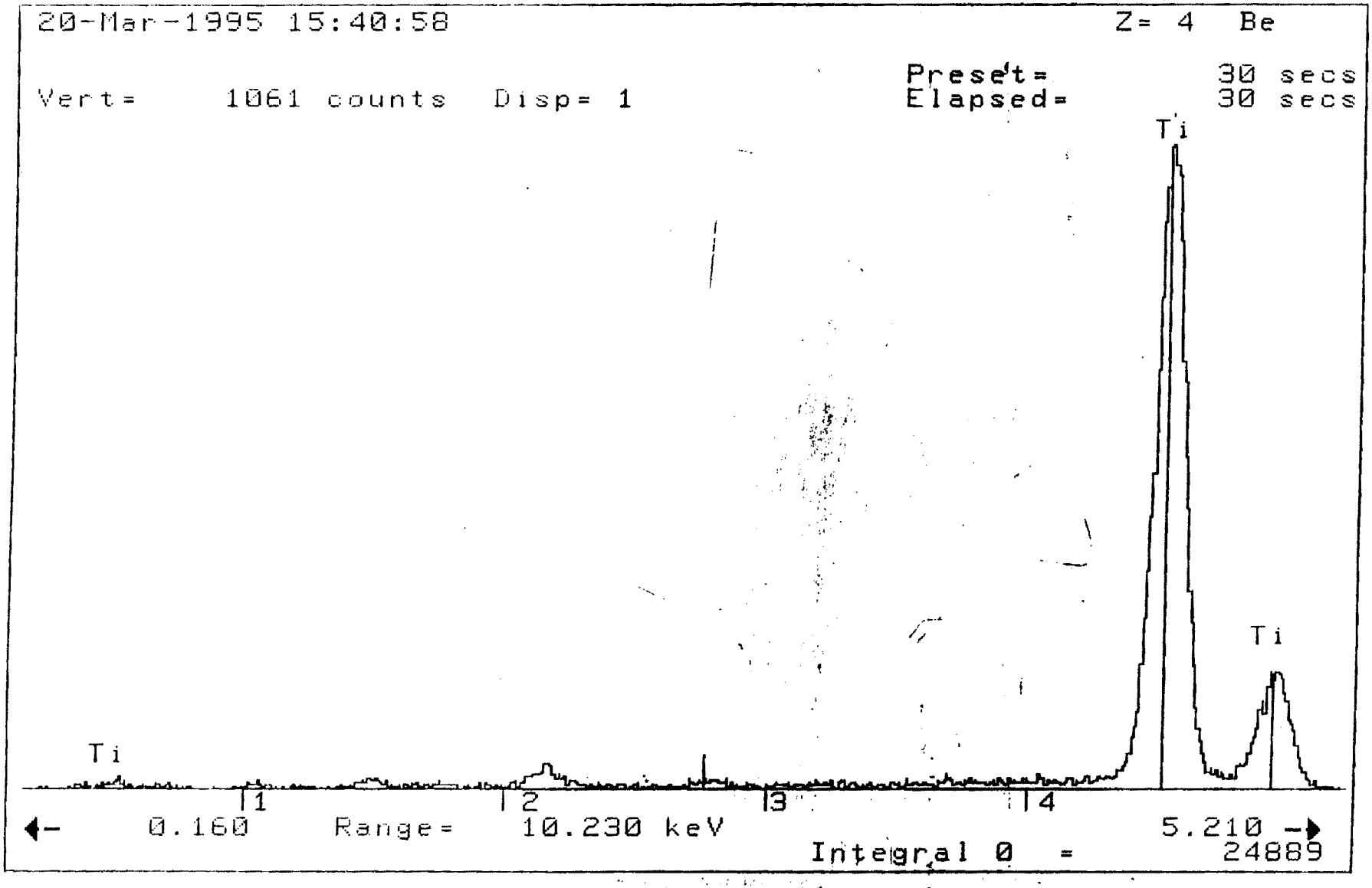

20-Mar-1995 15:26:37
Vert= 937 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
Ti
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 19702

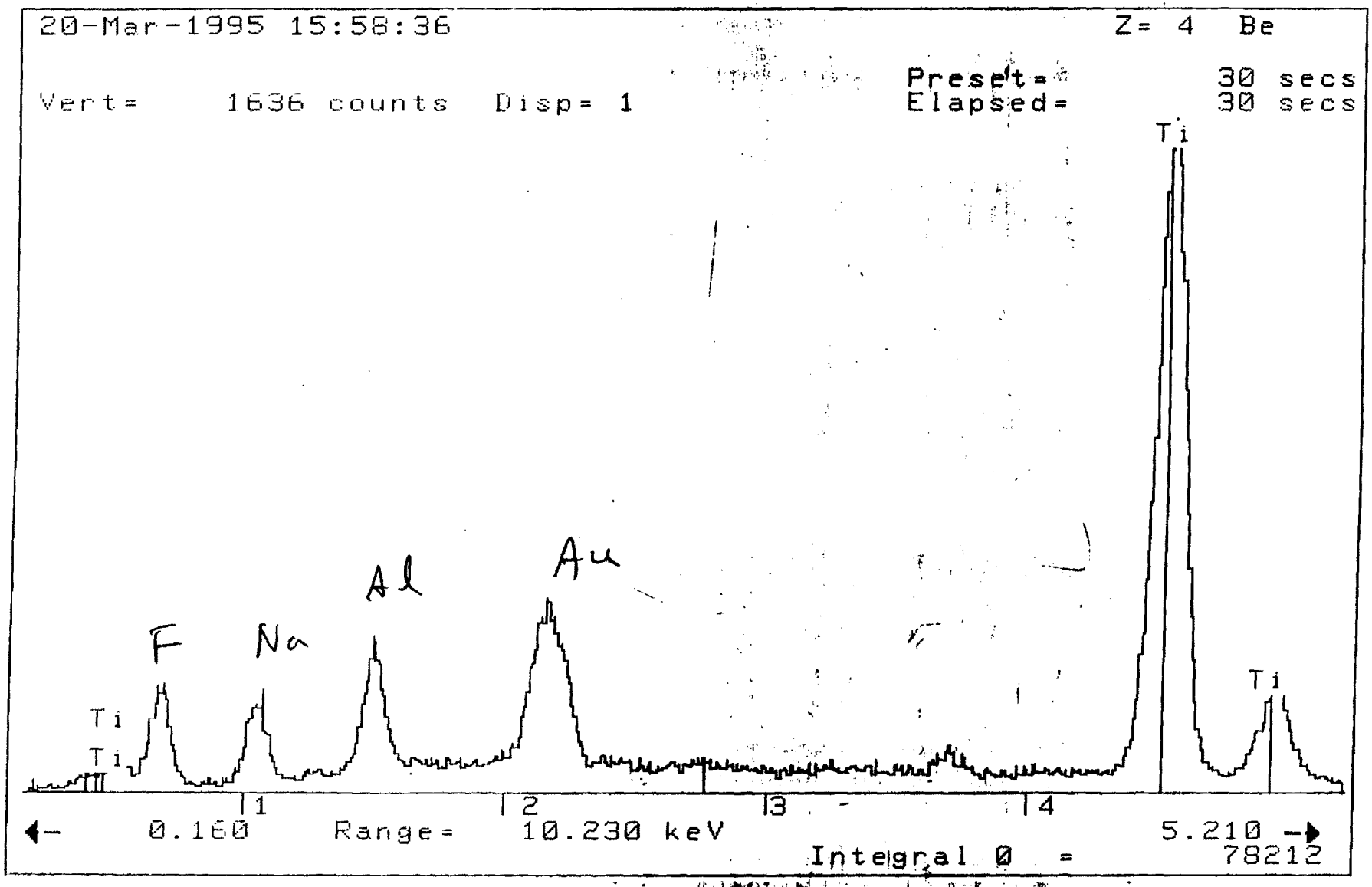

20-Mar-1995 15:29:40
Z= 4 Be
Preset= 30 secs
Elapsed= 27 secs
Vert= 3277 counts Disp= 1
Ti
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 105292

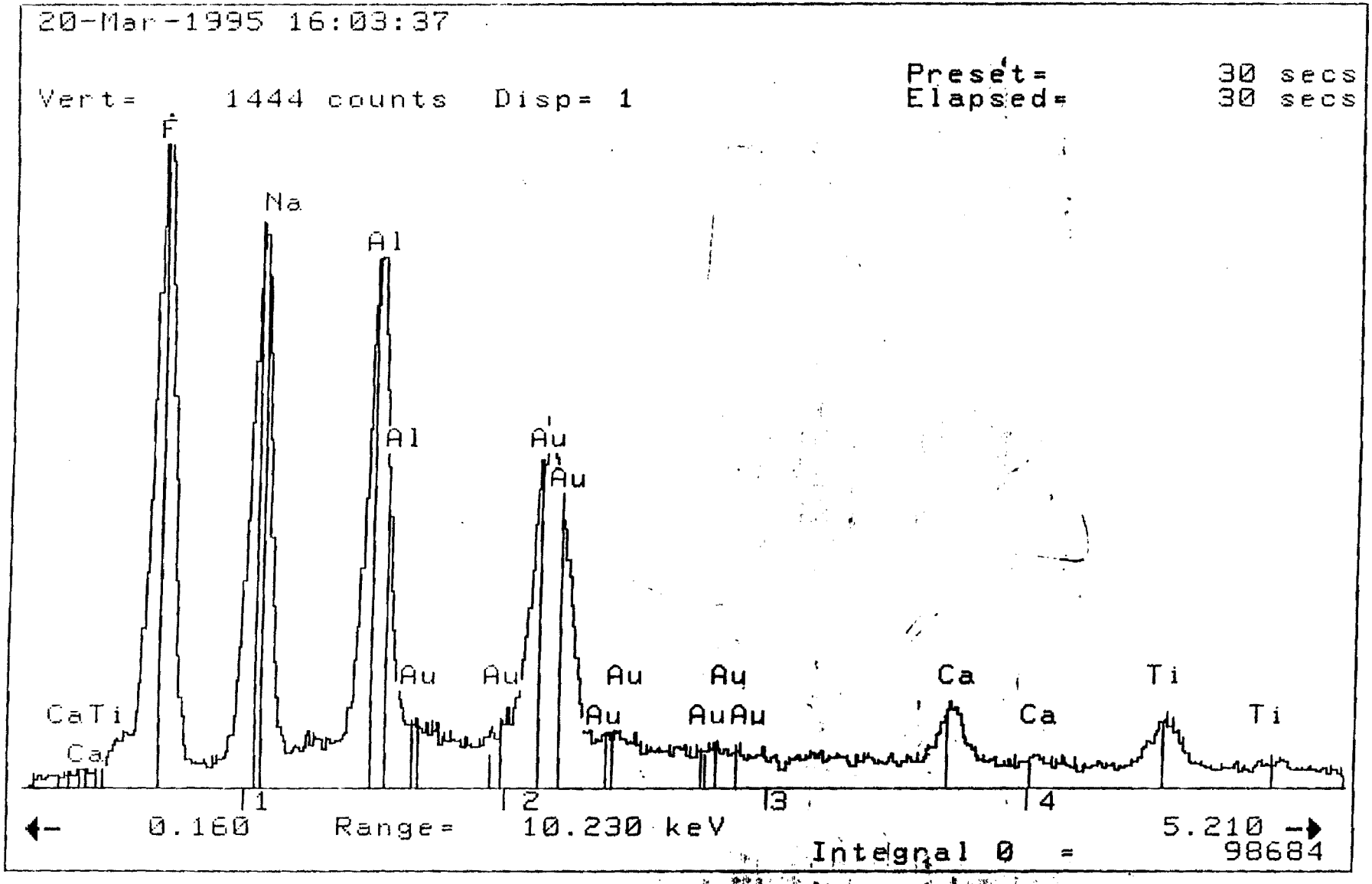

20-Mar-1995 15:37:04
Z= 4 Be
Preset= 30 secs
Elapsed= 27 secs
Vert= 446 counts Disp= 1
Ti
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 10797

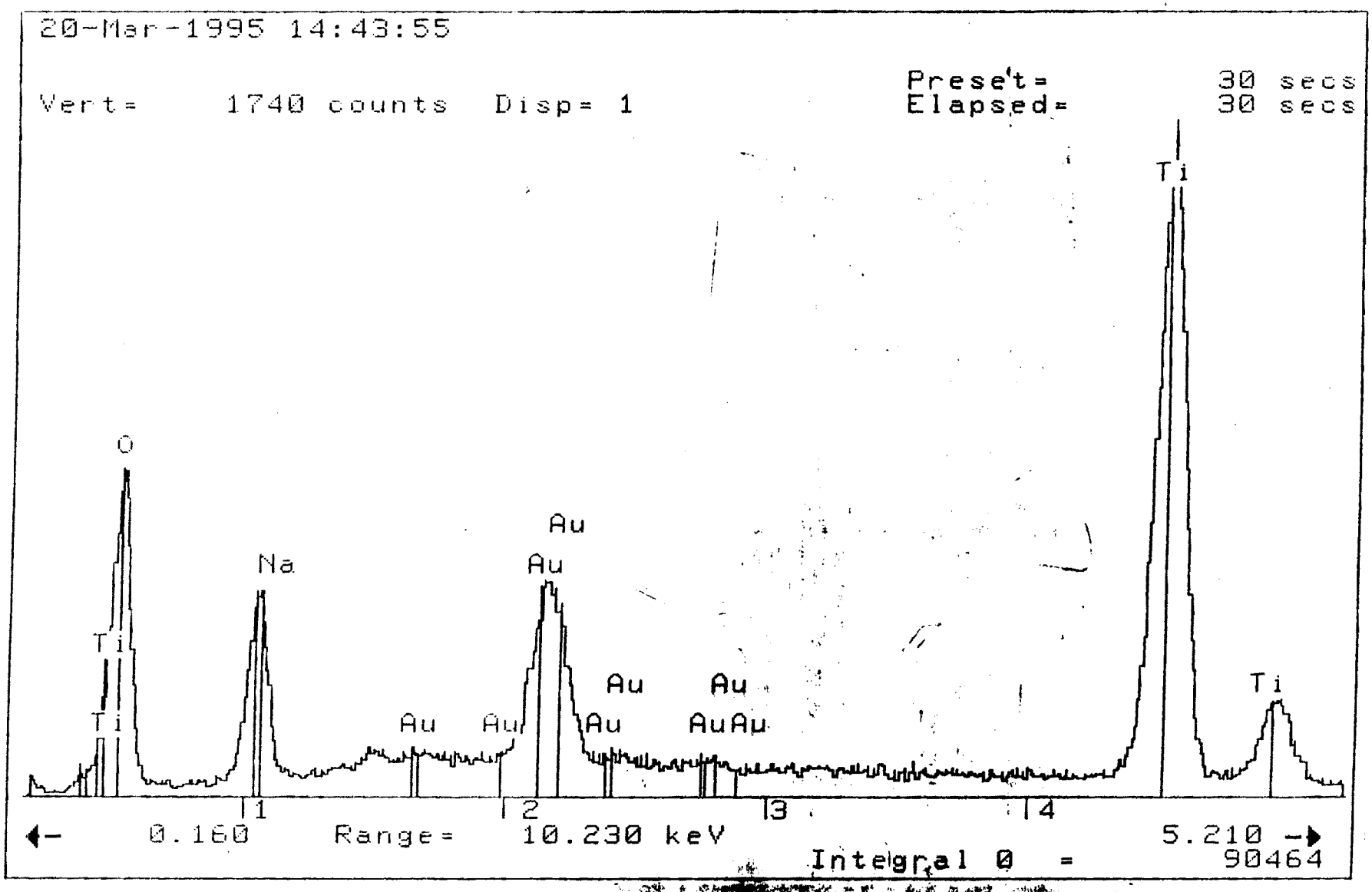

20-Mar-1995 15:22:18
Vert= 52 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
Ti
Al
Ti
Na
Al
F
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 2430

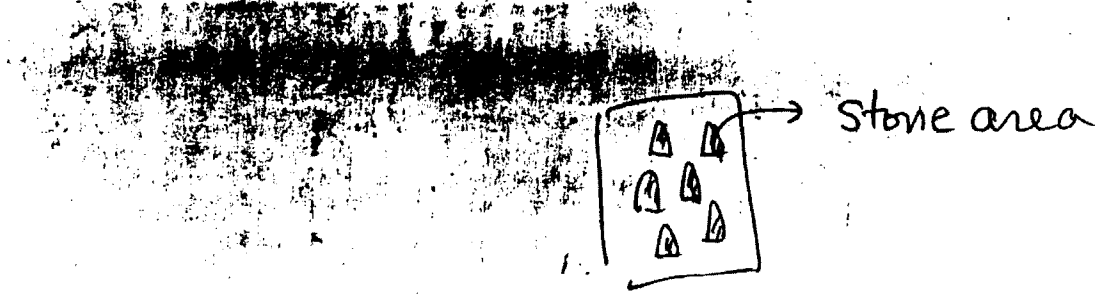

20-Mar-1995 15:43:25
Z= 4 Be
Vert= 1663 counts Disp= 1
Preset= 30 secs
Elapsed= 23 secs
Ti
Au
Al
Na
F o
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 70126

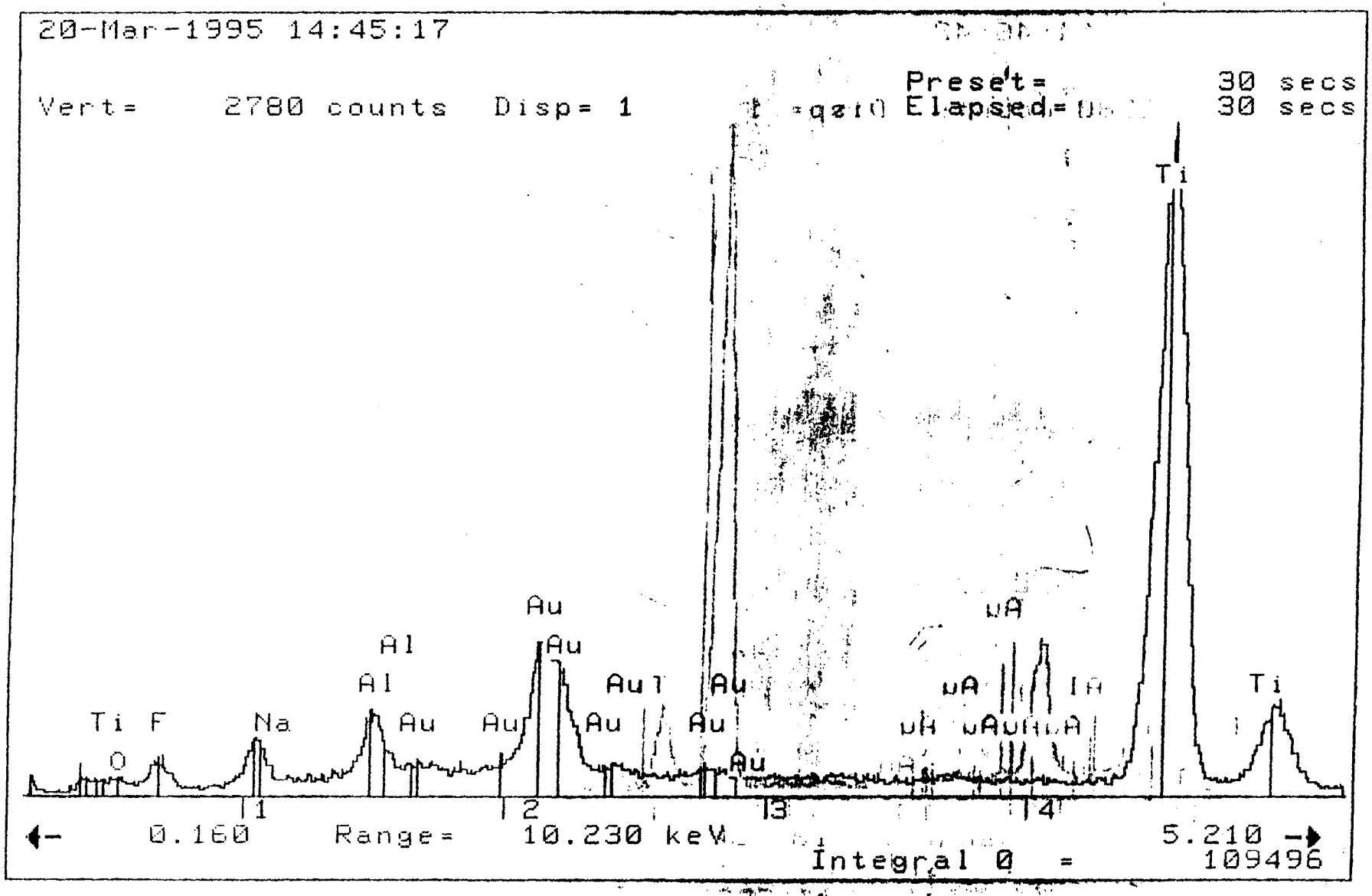

20-Mar-1995 15:40:58
Z= 4 Be
Preset= 30 secs
Elapsed= 30 secs
Vert= 1061 counts Disp= 1
Ti
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 24889


20-Mar-1995 15:58:36
Z= 4 Be
Vert= 1636 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
Ti
F
Na
Al
Au
Ti
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 78212


20-Mar-1995 16:03:37
Vert= 1444 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
F
Na
Al
Al
Au
Au
Au
Au
Au
Au
Au
Au
Au
Ca
Ca
Ti
Ti
CaTi
Ca
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 98684


20-Mar-1995 14:43:55
Vert= 1740 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
O
Ti
Ti
Na
Au
Au
Au
Au
Au
Au
Au
Au
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 90464


Stone area



general matrix area

XRD Characterization of Leaching Product by Scaled Up Process

February 24, 1995

By Hyunho Shin

I. Introduction

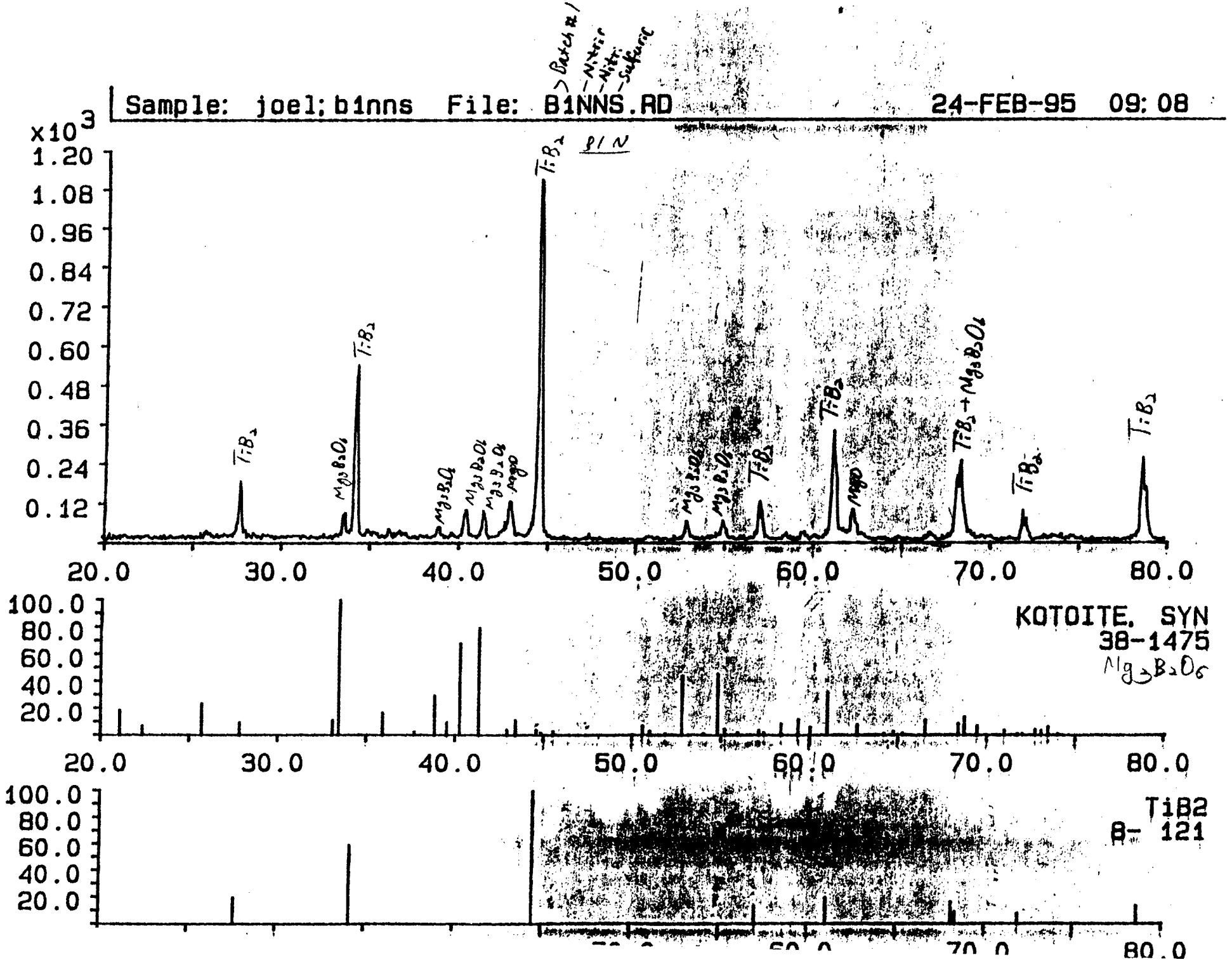
The chemical leaching process has been scaled up at 78-H building from 430 grams to 7500 grams (for the first run). Equivalent amount of nitric acid and sulfuric acid has been used. The leaching product needs to be characterized to check the integrity of the first run of the scaled up process.

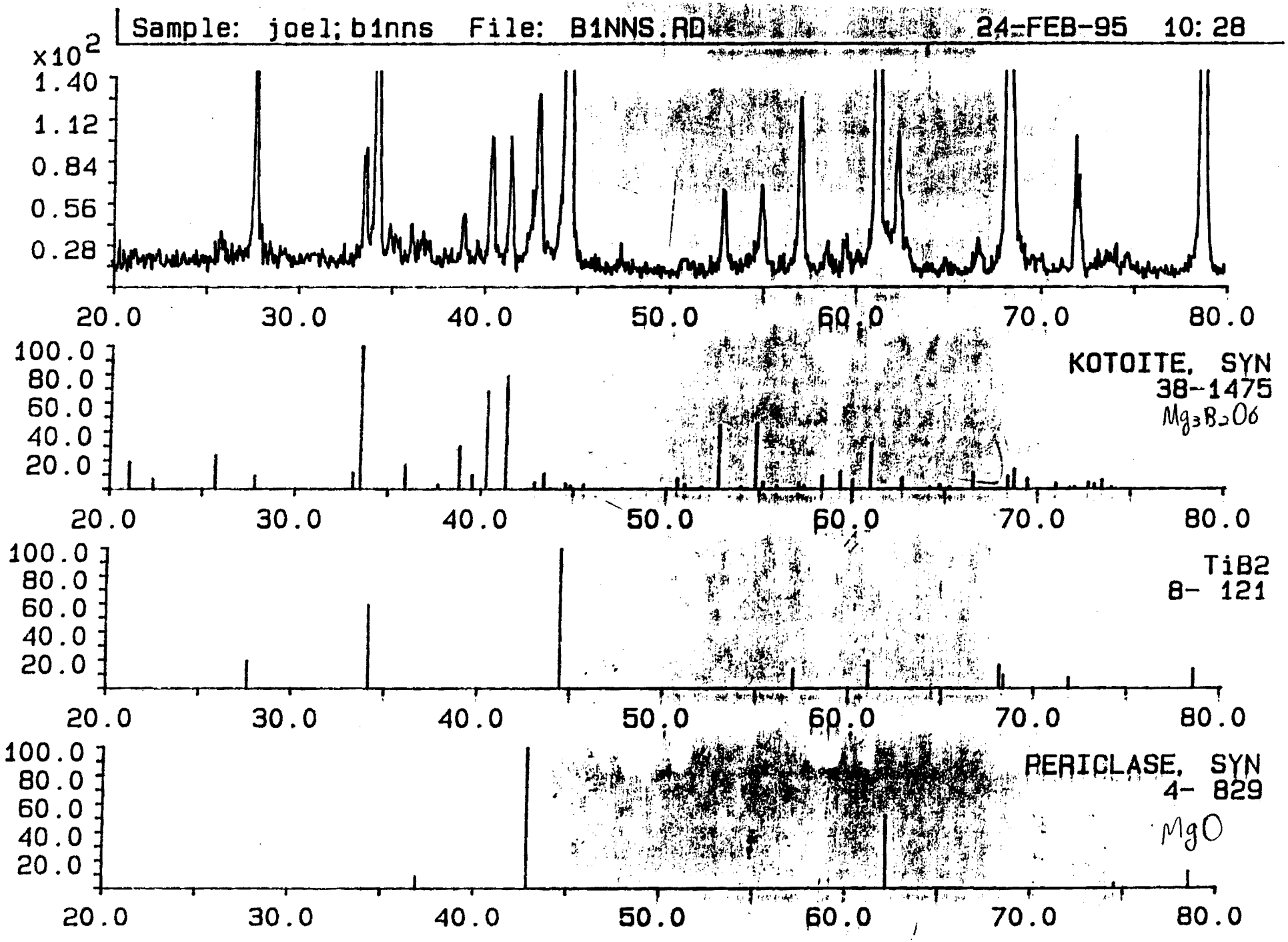
II. Experimental Procedure

As-received (from Joel) sample was further pulverized using a mortar and pestle. XRD step size was 0.02° with duration time of 1 sec at each step.

II. Results

As shown in the attached XRD pattern, the leached product contained MgO as well as Mg3B2O6 in addition to TiB_2, indicating that the leaching has not been completed. Further modification of the scaled up process is required.


Sample: joel; b1nns File: B1NNS.RD 24-FEB-95 09:08
x10 3
1.20
1.08
0.96
0.84
0.72
0.60
0.48
0.36
0.24
0.12
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KOTOITE, SYN
38-1475
100.0
80.0
60.0
40.0
20.0
TiB2
B- 121


Sample: joel;b1nns File: B1NNS.RD 24-FEB-95 10:28
x10 2
1.40
1.12
0.84
0.56
0.28
20.0
30.0
40.0
50.0
60.0
70.0
80.0
100.0
80.0
60.0
40.0
20.0
KOTOITE, SYN
38-1475
Mg3B2O6
TiB2
8- 121
PERICLASE, SYN
4- 829
MgO

Characterization of Residual Refractory Fragments After Chemical Leaching

February 24, 1995
by Hyunho Shin

I. Introduction

The chemical leaching system has been scaled up at 78-H building. Instead of 430 grams of as-reacted powder (for pure TiB2), 7500 grams of powder with an appropriate volume of nitric acid has been used (for the first and second wash). For the sulfuric wash, however, leaching method has been slightly modified --- instead of pouring 10 vol % sulfuric acid solution into a dilute water-powder slurry, the acid solution has been poured directly to the powders in a filtration funnel. This modified process caused a fervent reaction generating excess heat and fumes. During a process to find clues for the cause of this violent reaction, several refractory fragments (2-5 mm in diameter) have been observed in the nitric acid leached powder. While other clues rtesponsible for the reaction are being investigated, identification of the unusual refractory particles are intended to be characterized.

II. Experimental Procedure

Five fragments were adhered to a disk type specimen stage using a double stick tape and then gold coated by a sputtering in a vacuum chamber (1hr). SEM and EDS analyses were performed (2.5hr).

III. Results

A schematic drawing of the five fragments are shown in Figure 1 with an SEM micrograph of fragment number 1, 3, and 4.
The EDS result from each fragment is shown in the following spectra.
As apparent in the spectra, all the fragments contained appreciable silicon element (sometimes silicon is the most predominant element) with magnesium, titanium, and oxygen. These fragments are interpreted to contain magnesium silicate ($MgSiO_4$) phase. It is speculated that the silicon element is originated from the fused cast silica container wall.
As the scaled up process required many batches of as-reacted powder, there probably had been a batch with unusual amount of silica container component. The magnesium silicate is thought to be formed during the thermite reaction. While the fragments are characterized, it should be noted that there is no direct evidence that these fragments are primarily responsible for the violent reaction during sulfuric wash.

Figure 1

(1)

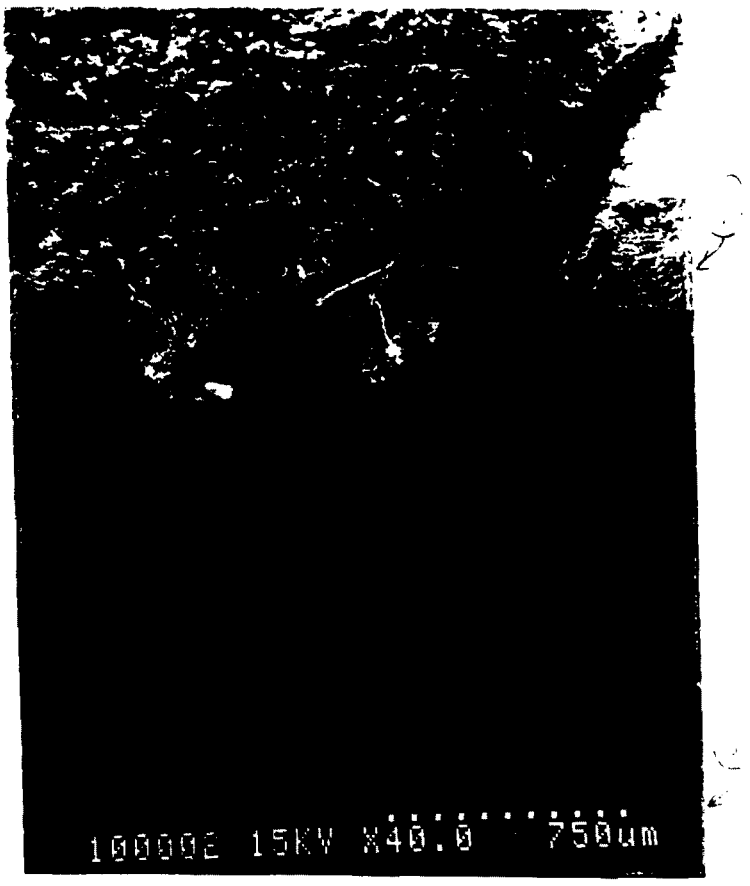
(4) Very large.

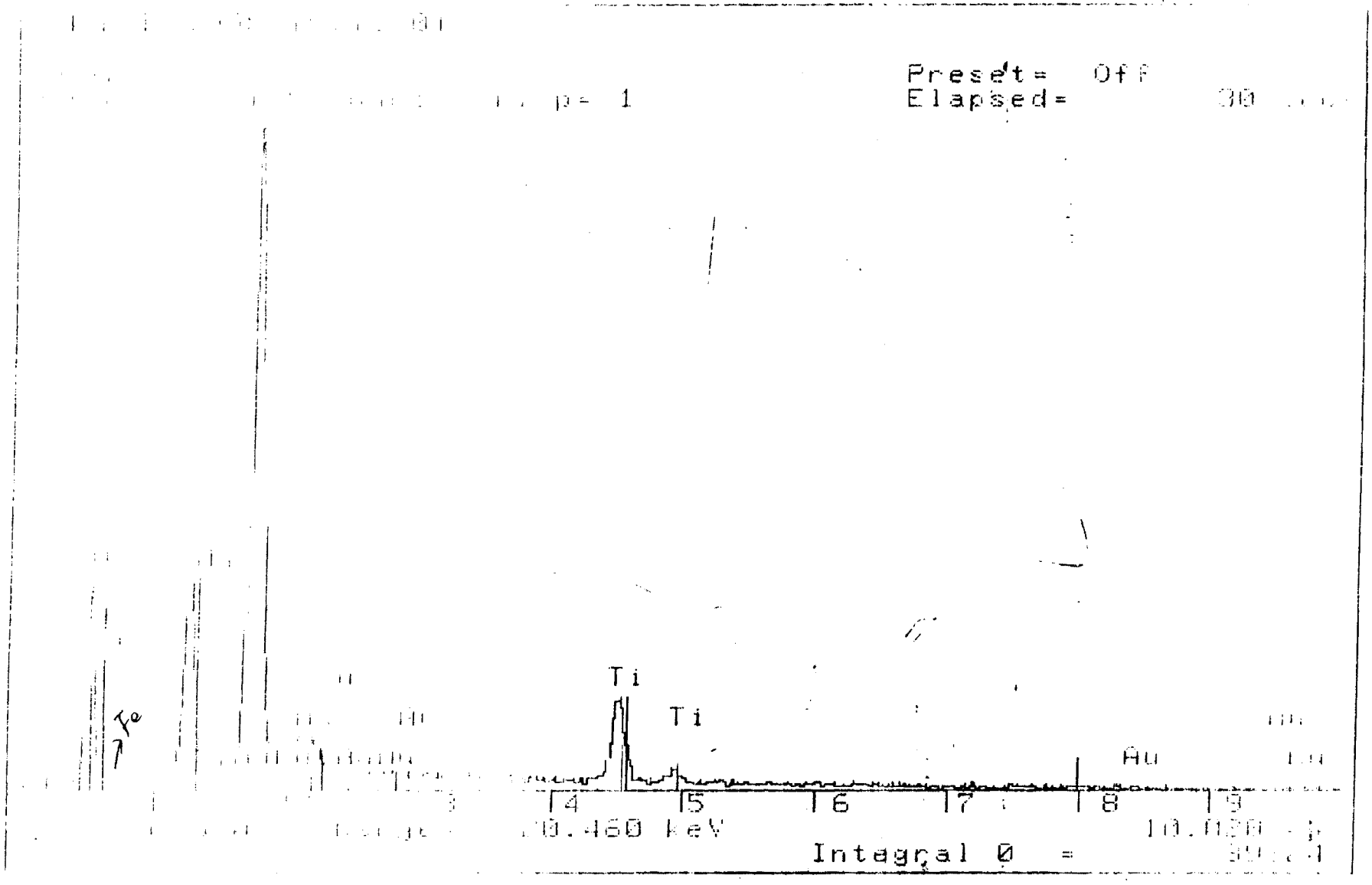
largest fine particles make a chunk

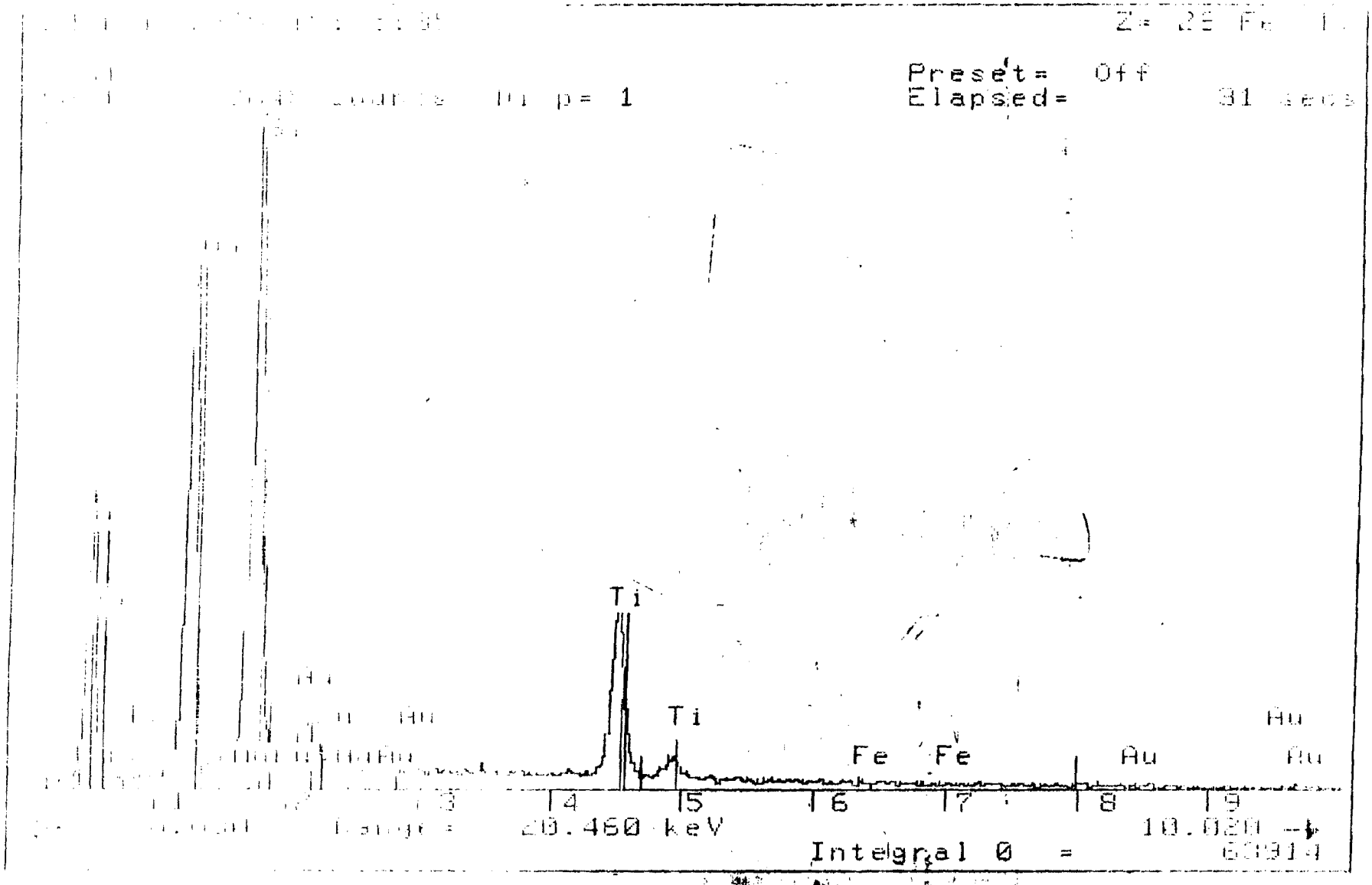
(3)

porous structure

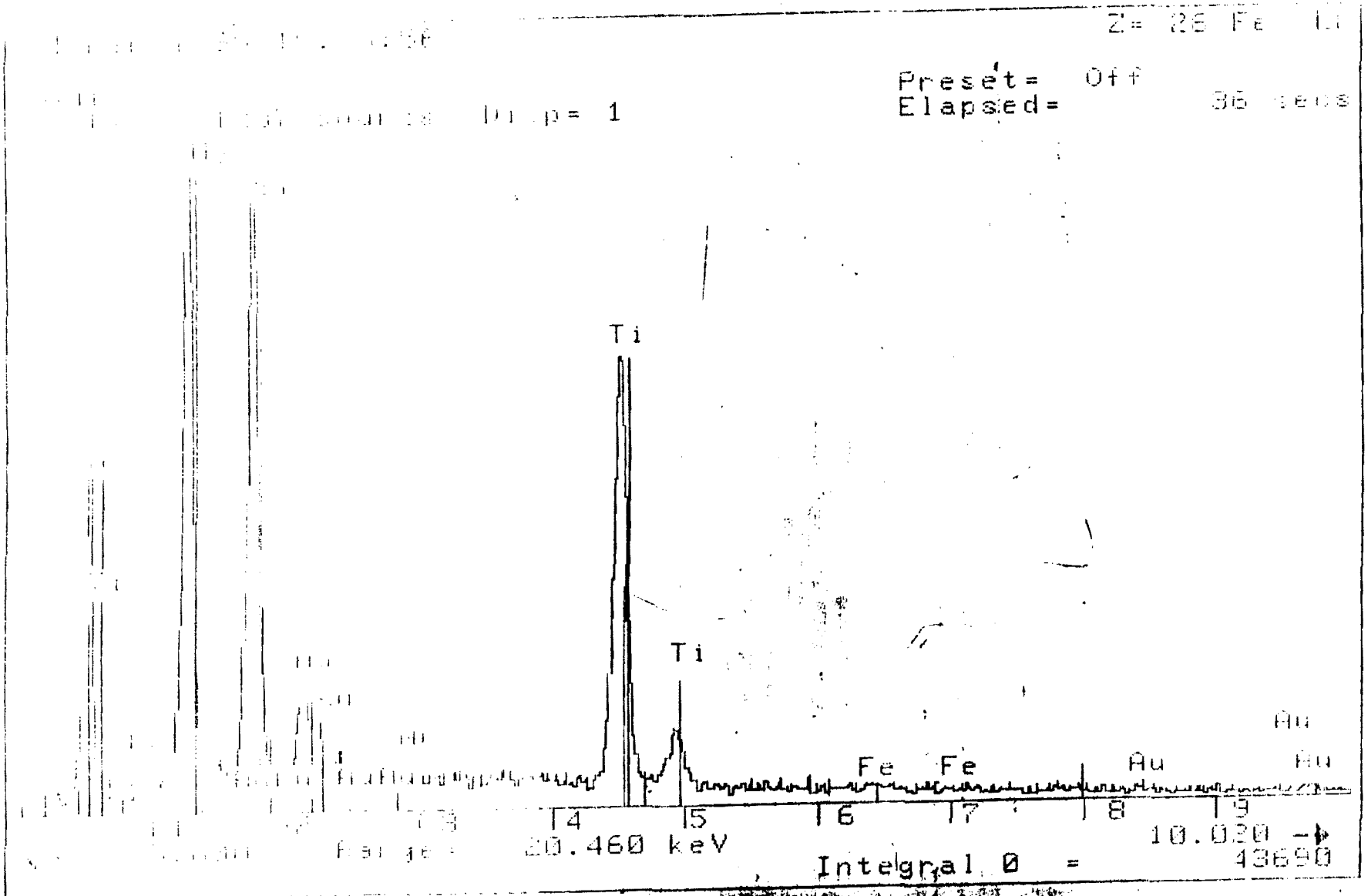
±12




Preset= Off
Elapsed=
Fe
Ti
Ti
Au
4
5
6
7
8
9
keV
Integral 0 =


Preset= Off
Elapsed=
31
p= 1
Ti
Ti
Fe
Fe
Au
Au
Au
4
5
6
7
8
9
20.460 keV
10.020
Integral 0 =

(3)


Z= 26 Fe
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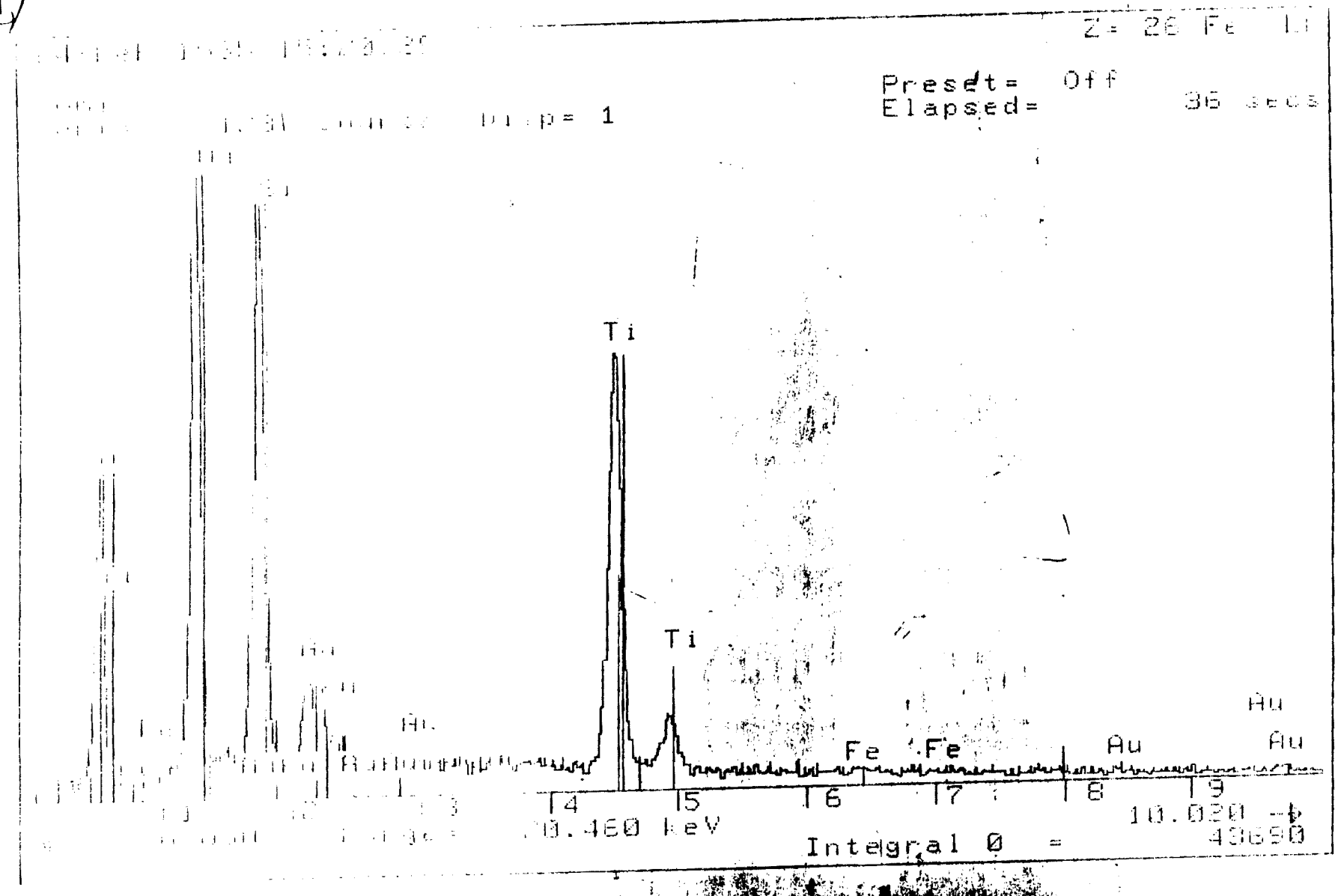
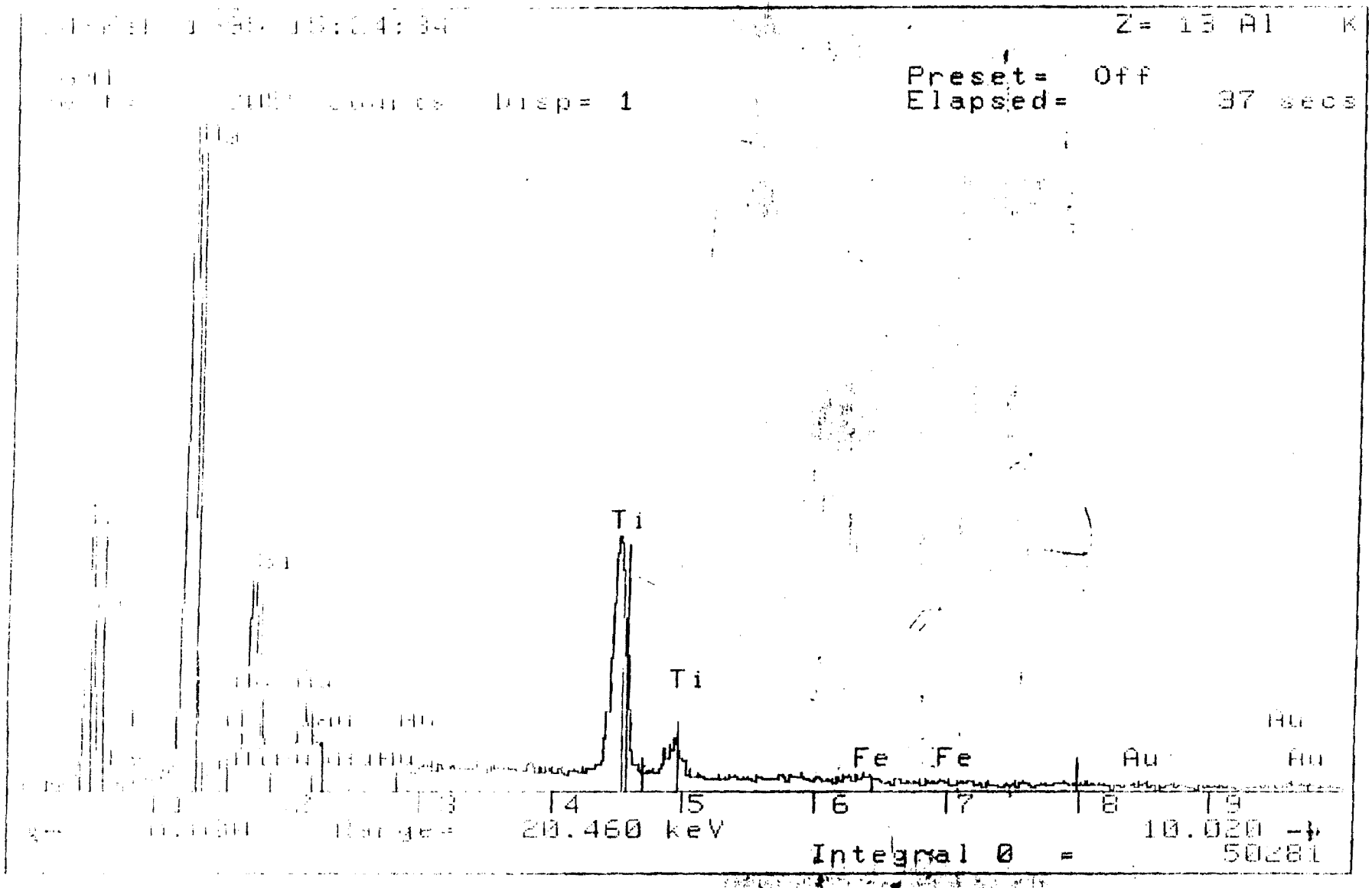
Elapsed=
Ti
Ti
Fe
Fe
Au
Au
Au
4
5
6
7
8
9
20.460 keV
10.020
Integral 0 =
43690

(4)


Z= 26 Fe
Preset= Off
Elapsed=
Ti
Ti
Au
Fe
Fe
Au
Au
4
5
6
7
8
9
10.020 keV
Integral 0 =

(5)


Z= 13 Al K
Preset= Off
Elapsed= 37 secs
Ti
Ti
Fe
Fe
Au
Au
Au
3
4
5
6
7
8
9
20.460 keV
10.020
Integral 0 = 50281

AEM PROJECT 3-9-95

SUMMARY OF PROGRESS REPORT

TiB_2/Al_2O_3 COMPOSITE

1 SHS Reactions

A total of 82 reactions have been completed, producing approximately 67.94 lb of T/A powder. All of the reactions, except for two, contained 400gm of TiO_2, B_2O_3, and Al powder mixed together. The basic mixture is 400g of mixed powder with a soichiometric ratio based on the stoichiometric reaction that will result in a TiB_2/Al_2O_3 composite.

$$3TiB_2 + 3B_2O_3 + 10Al = 3TiB_2 + 5Al_2O_3$$

	stoich (g)	actual (g)
TiB_2	133.48	133.60
B_2O_3	116.28	116.00
Al	150.20	152.40
Total	399.96	402.00

Analysis of the reacted powder indicates the composite powder contains TiB_2 and Al_2O_3. The Composite Batch Table summarizes all 82 composite reactions.

2 Ball Milling

The material was ball milled in the lab for 8hr, 15hr, and 30hr in a ball mill using alumina balls as a grinding media. Approximately 21.90 lbs. of ball milled powder was produced.

Ball mill (hr)	**gm**	**lb**
8	6151.72	13.55
15	1907.94	4.20
30	1886.24	4.15
Total	9945.90	21.90

In addition to the lab ball milling, approximately 14.9 lbs. was milled by Union Process. The ball mill inventory is shown in Table 3a.

3 T/A Powder Inventory

3a. Total SHS powder produced (82 reactions) = 74.77lb

	gm	lb
Unmilled	17242.15	37.98
Milled (Ga Tech)	9945.90	21.90
Milled (Union Process)	6754.80	14.90
Total	33943.57	74.77

3b. Submitted to AEM:

i	John Winters	420.00	0.90
ii	John Winters (8hr ball mill)	3364.14	7.41
iii	Steve Beers (Union Process)	4844.20	10.70

3c. Submitted to Union Process:

Unmilled powder	11032.20	24.30

3d. Inventory on Hand:

Milled (Lab)		
8hr	913.90	2.45
15hr	1420.00	3.13
30hr	282.00	0.62
Unmilled Powder	3296.70	7.26
Milled (Union Process)	1906.80	4.20

(Note: We will update the inventory once we receive the 24.30 lbs. of powder submitted to Union Process for milling.)

4 Disk Inventory

We have produced 11 disks; 7 from 8 hr. milled powder and 4 disks from 30 hr. milled powder. We have submitted 5 disks to AEM; 3 disks (#1,#2,#4) from 8 hr. ball milled powder and 2 disks (#10, #11) from 30 hr. ball milled powder. Today (3-8-95), as per John Winters request, the rest of the disks have been submitted to Joel Tenny. We have no disks in the lab.

5 Hot Pressing

Seven 3"dx1/2"t disks were hot pressed using 8hr ball milled powder and four 3"dx1/2"t disks were hot pressed using 30hr ball milled powder.

CTP curves were obtained for disks #9 and #10, which used 30hr ball milled powder. The hot pressing parameters are summarized in the Hot Press Table and the CTP curves for disks 9 and 10 attached.

Both the final pressure and the temperature are key parameters for hot pressing the composite disks. With the maximum pressure (6500psi) applied to POCO XT graphite, the temperature is the only parameter that can be varied to obtain a density greater than 97.5%. Based on the analysis of the CTP curves it is possible to obtain a density greater than 97.5% with a higher temperature than 1580°C.

AEM PROJECT 3/7/95
COMPOSITE BATCHES

BATCH	MASS	PERCENT	BALL MIL	PART	XRD
1	357.2	89.30			YES
2	374.92	93.73			
3	374.92	93.73			
4	374.92	93.73	FAIL 30		
5	374.92	93.73	FAIL 15		
6	374.92	93.73	HR 8		YES
7	374.92	93.73	HR30		YES
8	374.92	93.73	HR 15		YES
9	366.2	91.55			
10	364.2	91.05			
11	367	91.75			
		0.00			
12	366	91.50			YES
		0.00			
13	378.1	94.53			YES
14	373.7	93.43			
15	378.4	94.60			
16	382.5	95.63			
17	378.1	94.53			
18	381.4	95.35			
19	364.1	91.03			
20	386.5	96.63			
21	381	95.25			
22	382.4	95.60			
23	359.9	89.98			
24	384	96.00			
25	363.6	90.90			
26	370	92.50			
27	382.2	95.55			
28	381.7	95.43	HR 8	1144.6	
29	381.7	95.43	HR 8		
30	381.2	95.30	HR 8		
31	389	97.25			
32	374.9	93.73			
33	385.4	96.35			
34	390.4	97.60			

35	362.1	90.53						
36	375.2	93.80	HR 8	3437.9				
37	381.2	95.30	HR 8	1144.6				
38	373.2	93.30	HR 30	4581.5				
39	378.3	94.58	HR 30					
40	386.9	96.73	HR 15					
41	387	96.75	HR 8					
42	384.9	96.23	HR30		BALL MILL			
43	386.7	96.68	HR 15		3873.3			
44	384.5	96.13	HR 15	3437.9				
45	385.5	96.38	HR 8					
46	386.9	96.73	HR 8					
47	386.4	96.60	HR 8					
48	392.3	98.08	HR 8					
49	384.9	96.23	HR 8					
50	388.8	97.20	HR 8					
51	385.5	96.38	HR 8		union milled			
52	388	97.00	HR 8		6755.52	14.88		
53	390.5	97.63	HR 8		gt milled			
54	575.8	143.95			9945.9	21.91		
55	386.4	96.60						
		0.00			8hr	15hr	30hr	
56	395	98.75			6151.72	1907.94	1886.24	
57	388.2	97.05			13.55	4.20	4.15	
58		0.00						
		0.00			total milled			
59	390.3	97.58			16701.42	36.79		
60	388.9	97.23						
61	386.9	96.73						
62	385.3	96.33						
63	385.1	96.28						
64	386	96.50						
65	390.8	97.70						
66	384.7	96.18						
67	391.3	97.83						
68	389.7	97.43						
69	391.1	97.78						
70	388.7	97.18						
71	392.8	98.20						
72	389.8	97.45						
73	380.1	95.03						
74	390.1	97.53						

75	391.2	97.80
76	388.5	97.13
77	385.1	96.28
78	390.8	97.70
79	388.3	97.08
80	390.3	97.58
81	385.7	96.43
82	578.2	96.37
	2624.431	

AVG MASS	AVG PERCENT
374.92	89.51

TOTAL MASS	
33943.57	74.77
unmilled	
17242.15	37.98

T/A HOT PRESS

PARAMETERS

RUN	TYPE POWDER	MASS (g)	DRY-PRESS (PSI)	FINAL-PRESS (PSI)	FINAL TEMP (C)	RAMP TIME (MIN)	SOAK TIME (HOURS)	THERMOCOUPLE TYPE
1	T/A COMP	240.0	3374	5399	1500		1:51	B
2	T/A COMP	239.7	3374	6298	1500	20	2:55	S
3	T/A COMP	239.8	3374	6501	1525	25	1:54	S
4	T/A COMP	239.9	3374	6501	1580	35	1:35	S
5	T/A COMP	239.8	3374	6501	1580	24	NA	S
6	T/A COMP	239.8	3374	6501	1580	20	2:10	S
7	T/A COMP	239.8	3374	6501	1580	25	2:50	S
8	T/A COMP	239.8	5624	5624	1580	22	3:08	S
9	T/A COMP	240.0	4499	6501	1580	25	1:00	S
10	T/A COMP	239.0	4499	6501	1580	60	0:55	S
11	T/A COMP	239.0	1125	6501	1580	65	2:35	S

T/A HOT PRESS

DISK DATA

DISK	DIMENSIONS DIAMETER (IN)	DIMENSIONS THICKNESS (IN)	GROSS MASS (g)	NET MASS (g)	THEORETICAL DENSITY (G/CM3)	TRUE DENSITY (G/CM3)	PERCENT DENSE
1	3	0.545	240.0	238.50	4.14	3.79	91.55
2	3.0465	0.55	239.7	238.13	4.14	3.72	89.86
3	3.039	0.512	239.8	233.79	4.14	3.93	94.93
4	3.041	0.495	239.9	233.50	4.14	4.04	97.58
5	3.048	0.612	239.8		4.14		
6	3.053	0.543	239.8	236.51	4.14	3.80	91.79
7	3.041	0.473	239.8	222.46	4.14	3.96	95.65
8	3.		239.8	224.70	4.14	3.93	94.5
9	3.	0.508	240.0	178.38	4.14	4.02	97.15
10	3.	0.496	239.0	178.55	4.14	4.04	97.60
11	3.	0.500	239.0	178.00	4.14	4.03	97.30

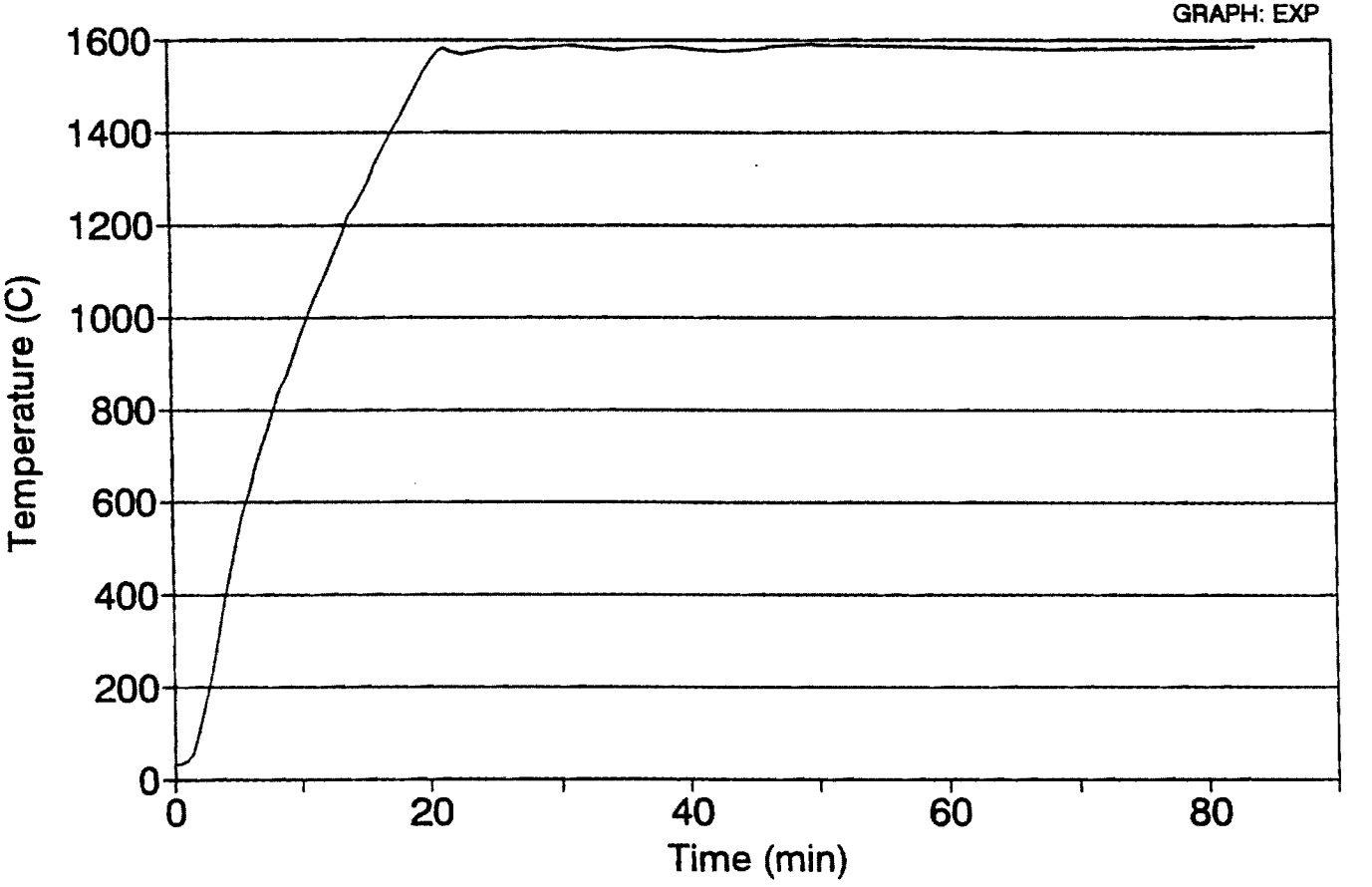
NOTES:
Run 1 to 5 - POCO PGCS-3 Dies
Run 6 to 11 - POCO XT Dies
Run 1 to 7 - 8 hr. ball mill powder
Run 8 to 11 - 30 hr. ball mill powder

TiB2-Al2O3 Disk #9

(Hot press #12)

FILE: EXPANSIO

GRAPH: EXP

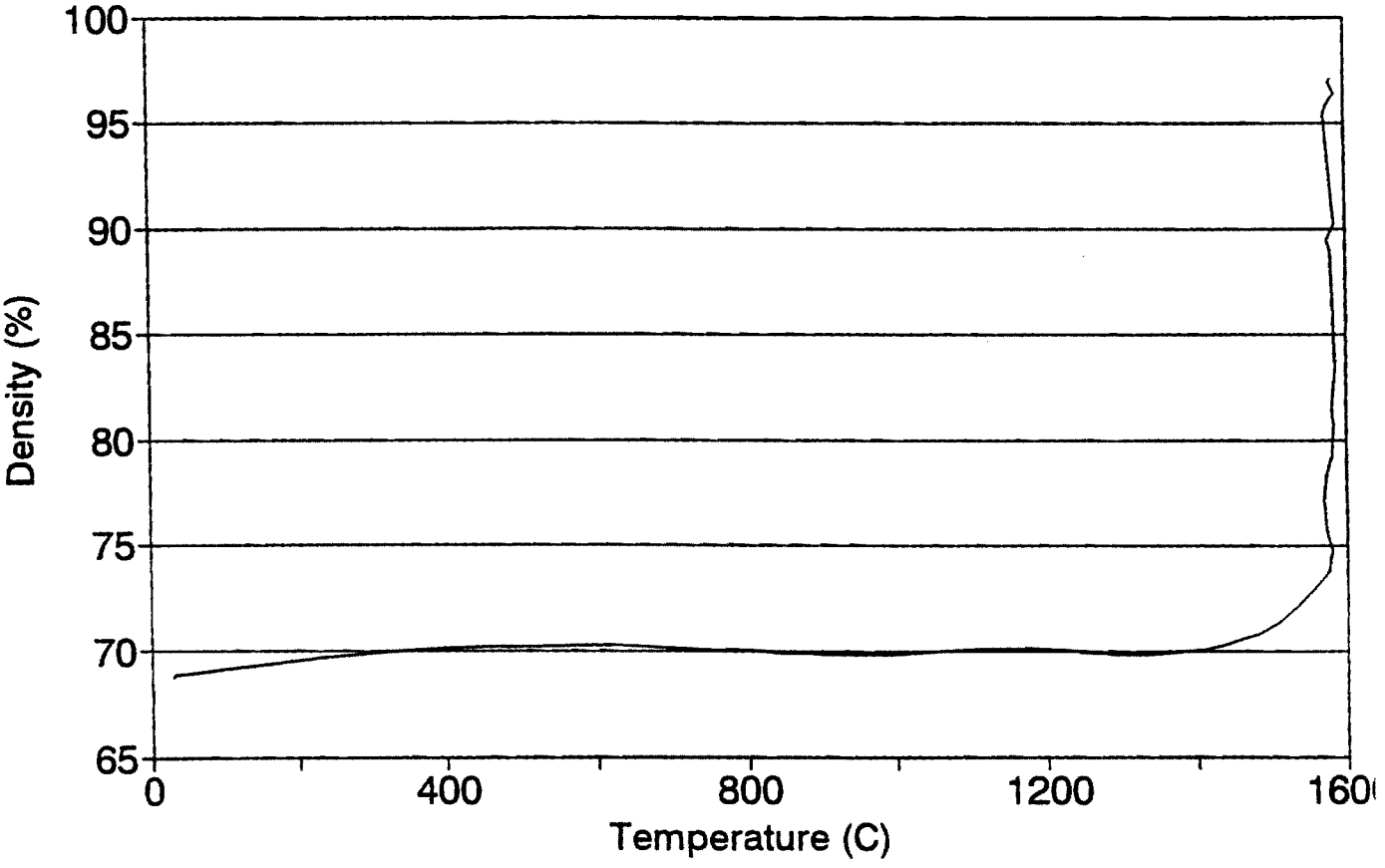


TiB2-Al2O3 Disk #9

(Hot press #12)

FILE: EXPANSIO

GRAPH: EXP

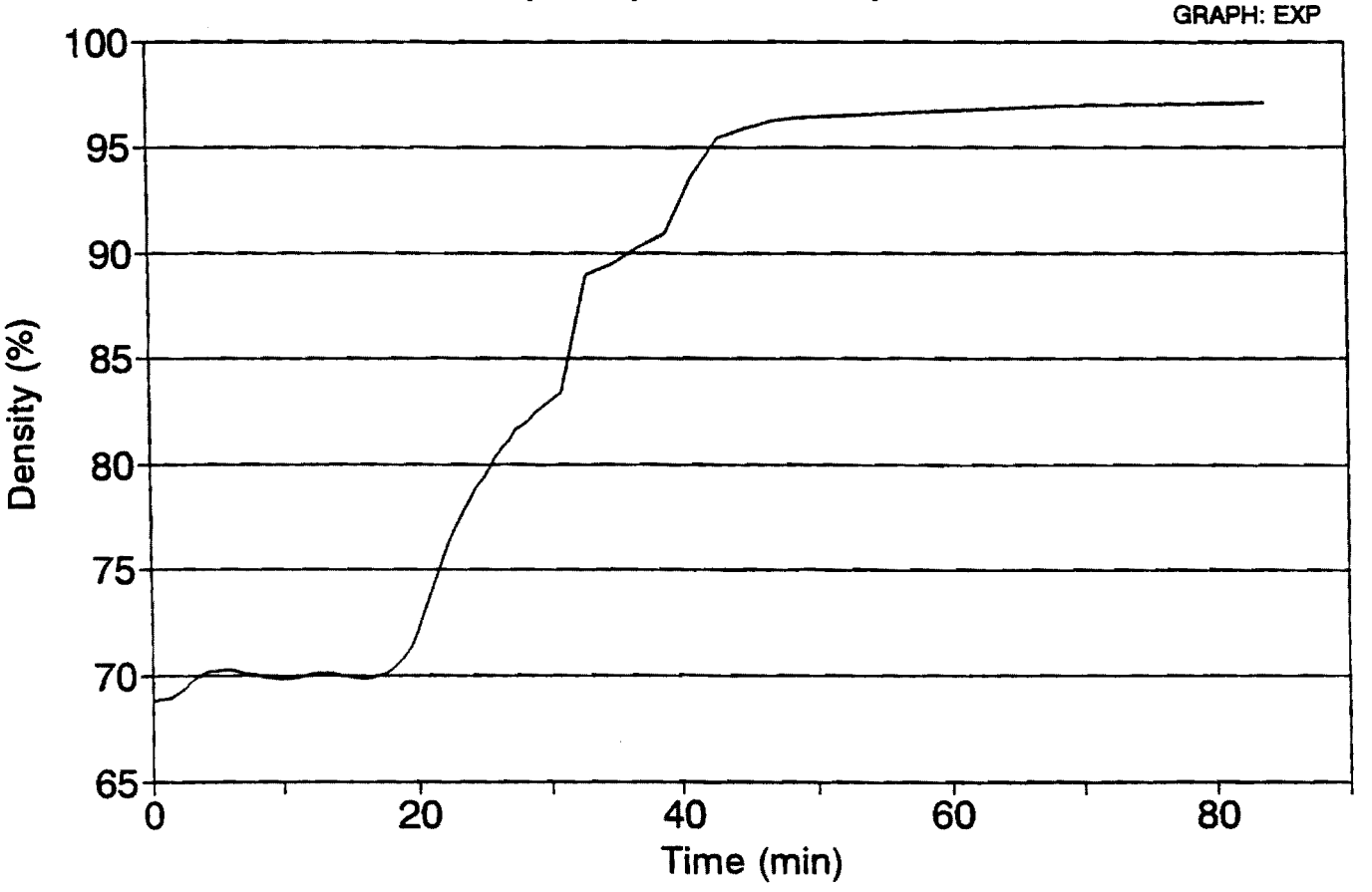


TiB2-Al2O3 Disk #9

(Hot press #12)

FILE: EXPANSIO

GRAPH: EXP

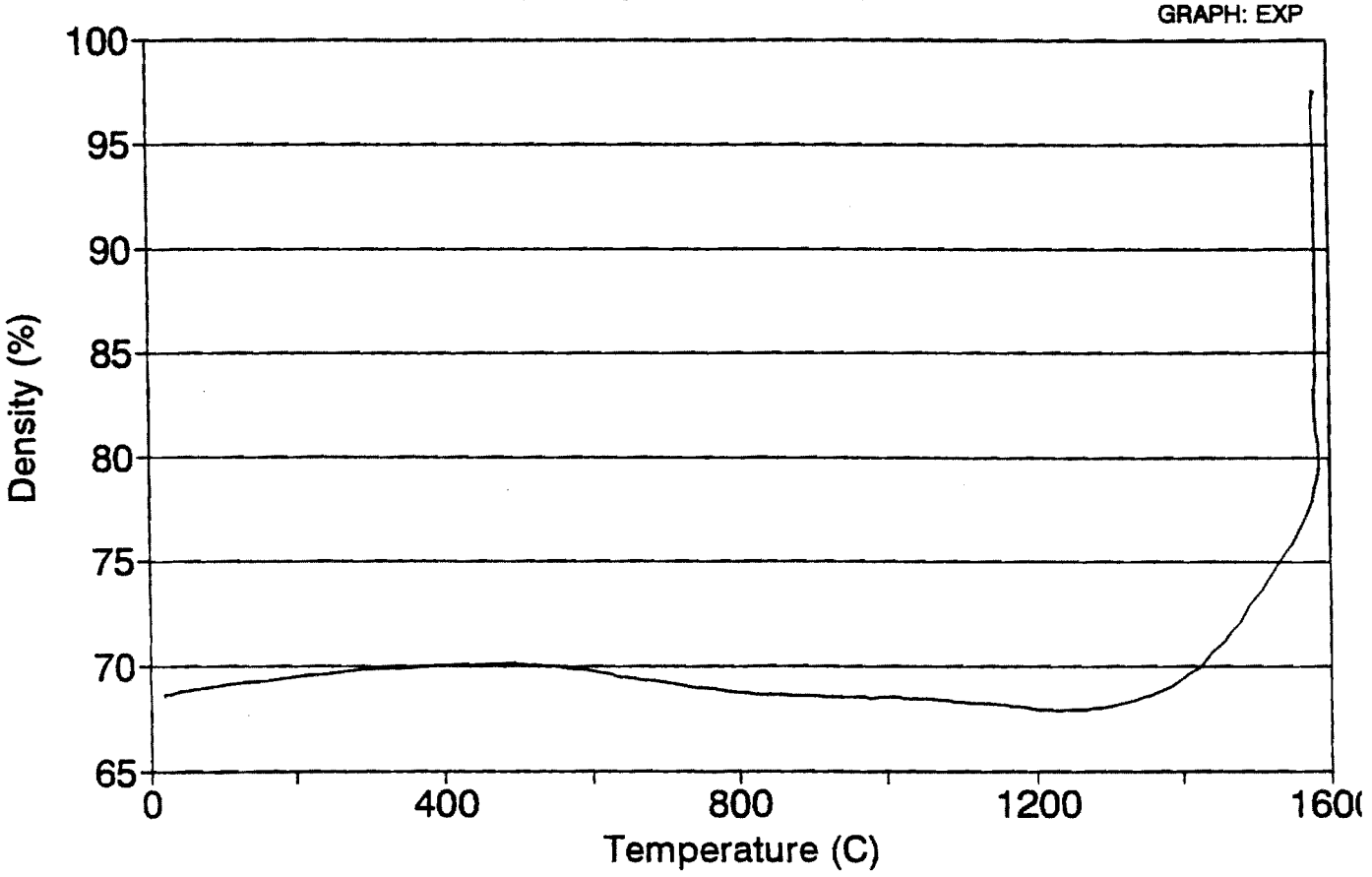


TiB2-Al2O3 Disk #10

(Hot press #14)

FILE: EXPANSIO

GRAPH: EXP

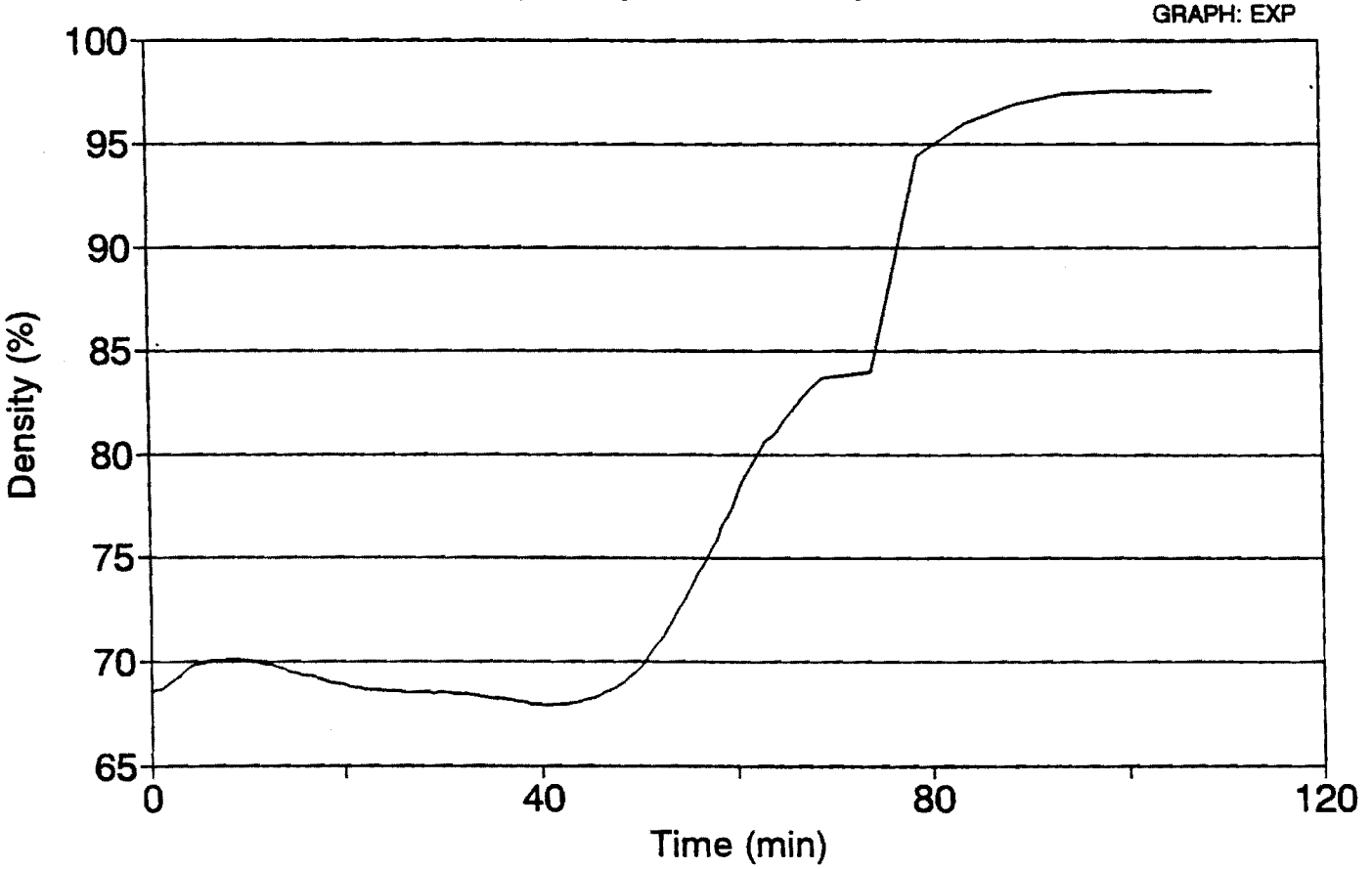


TiB2-Al2O3 Disk #10

(Hot press #14)

FILE: EXPANSIO

GRAPH: EXP

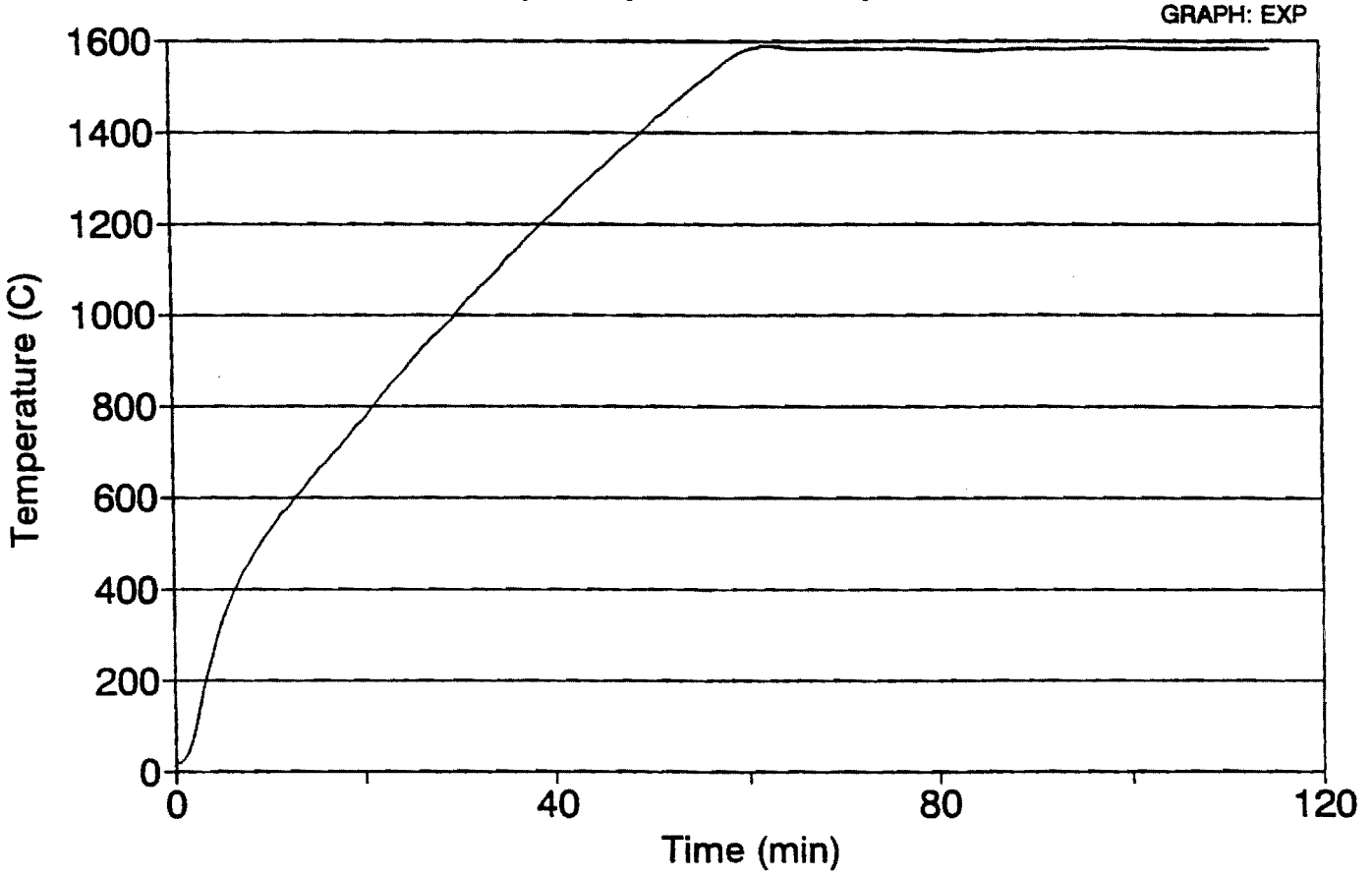


TiB2-Al2O3 Disk #10

(Hot press #14)

FILE: EXPANSIO

GRAPH: EXP



AEM PROJECT 3-9-95

SUMMARY OF PROGRESS REPORT

TiB_2

1 SHS Reactions

A total of 45 reactions have been completed with a yield of approximately 48.76lb of SHS TiB_2 powder. All 45 reactions are summarized in the TiB_2 Batches Table. In order to minimize the amount of titanates produced, the stoichiometry ratio was adjusted with excess B_2O_3 and Mg for all 45 reactions. A 600gm mixture containing TiO_2, B_2O_3, and Mg powders was reacted to produce TiB_2.

$TiO_2 + B_2O_3 + 5Mg = TiB_2 + 5MgO$

	Stoich (g)	actual (g)
TiO_2	133.70	133.70
B_2O_3	116.50	162.70
Mg	203.41	303.60
Total	453.61	600.00

2 Leaching

Prior to leaching, the pure TiB_2 material was ball milled in a steel ball mill for 30 minutes using steel balls as a grinding media. The leaching was performed as per the procedure established previously. However, the ph control and the sulfur washing steps have been modified to minimize the formation of compounds such as TiO_2 and Mg-titanates. Reactions 6 through 31 were leached in the lab in the manner described by the procedure. Each batch leached contained 430 g. of powder. During acid leaching the ph and the amount of HNO_3 used were varied and the sulfur washing steps were modified. The leached samples 1 through 15 were analyzed to determine at what ph level MgO, Mg-borates, Mg-titanates, and TiO_2 compounds could be minimized. The results are summarized in the Leaching Study Table.

SHS batches 32 through 45 have been leached in a large stainless steel tank designed by Joel Tenny. The results of the large leaching operation have not been completely evaluated.

3 Powder Inventory

3a. SHS Powder

	gm	lb
Total SHS powder	22139.30	48.76
Ball milled (lab, 30min)	19867.00	43.76
Union Process (milled)	2270.00	5.00

3b. Leached Powder

	starting wt gm	starting wt lb	leached wt gm	leached wt lb
i Leached batches 6 to 31 (batch process)	12332.00	27.16	2759.40	6.08
ii Batches 32 to 45 (bulk process steel tank)	7259.90	15.99	1700.00	3.75

3c. Inventory on hand

Union process ball mill (batches 1,2,3,4,5)	2270.00	5.00

(Note: This material has been given to Joel Tenny today, 3-8-95 for bulk leaching)

3d. Disk Inventory

A total of 2335.50gm of leached (lab) powder has been used to manufacture 7 hot pressed disks.

Disks 1, 2, 3, 5 and 6 have been submitted to Joel Tenny today (3-8-95) as per the request of John Winters. Disk no.4 was picked up by John Winters (1-23-95). We have one disk (#7) in possesion.

4 Hot Pressing

Leached material (SHS batches 6 to 31) was used to hot press TiB_2 disks. Six 3"d x 1/2"t disks and one 3"d x 0.4"t have been produced. CTP curves were obtained for disks 4 and 6. The hot pressing parameters are summarized in the Hot Press TiB_2 Table and

the CTP curves are attached. It appears from the CTP curves that the final pressure is not as critical as the final soak temperature for hot pressing TiB_2. The final soak temperature appears to be the key parameter for maximizing the density of the disk. Analysis of the CTP curves indicate that a temperature above 1650°C will be needed to obtain density of greater than 97%.

AEM PROJECT 3/7/95
PURE TiB2 BATCHES

BATCH	MASS GROSS	NET	% RETURN GROSS	NET
1		501.40		83.57
2		501.20		83.53
3		517.20		86.20
4		511.60		85.27
5		516.00		86.00
6	535.90	525.00	89.32	87.50
7	528.70	510.40	88.12	85.07
8	525.80	449.30	87.63	74.88
9	530.00	506.30	88.33	84.38
10	391.40	368.00	65.23	61.33
11	336.00	317.00	56.00	52.83
12	268.00	248.00	44.67	41.33
13	341.00	329.00	56.83	54.83
14	315.00	300.00	52.50	50.00
15	569.10	540.90	94.85	90.15
16	538.60	520.20	89.77	86.70
17	553.90	537.80	92.32	89.63
18	545.60	526.60	90.93	87.77
19	514.30	495.00	85.72	82.50
20	529.40	509.30	88.23	84.88
21	523.50	501.70	87.25	83.62
22	533.20	517.20	88.87	86.20
23	538.80	532.80	89.80	88.80
24	551.70	538.70	91.95	89.78
25	549.00	535.00	91.50	89.17
26	544.50	527.50	90.75	87.92
27	555.70	537.20	92.62	89.53
28	528.40	514.50	88.07	85.75
29	475.00	465.00	79.17	77.50
30	495.10	487.00	82.52	81.17
31	502.50	492.60	83.75	82.10
32	489.00	478.80	81.50	79.80
33	507.30	496.00	84.55	82.67
34	495.60	488.60	82.60	81.43
35	500.00	488.80	83.33	81.47
36	574.50	566.90	95.75	94.48
37	604.60	592.20	100.77	98.70

38	510.50	492.60	85.08	82.10
39	520.40	514.60	86.73	85.77
40	543.20	538.30	90.53	89.72
41	563.45	537.00	93.91	89.50
42	511.00	504.80	85.17	84.13
43	546	538	91.00	89.67
44	533.4	524.1	88.90	87.35
45	501.9	499.2	83.65	83.20

AVG GROSS	AVG NET	AVG GROSS %	AVG NET %
505.52	491.98	84.25	82.00

TOTAL	TOTAL-g	TOTAL-lb
20220.95	22139.3	48.76

40/50 GL
5/5 AL
UP
T
T/A

TO: K. V. Logan

FROM: Gautam Patel

SUBJECT: AEM Project
Progress Report (3-20-95 to 3-31-95)

DATE: 4-3-95

1 Ten more (10-19 S/S) TiB2 reactions using a new recipe (stoich + 5% excess B2O3) have been completed and ball milled for 30 minutes. This produces approx. 5069gm of ball milled powder. A sample has been collected for XRD.

2 First nine (1-9 S/S) SHS reactions produced approx. 4918gm. of ball milled TiB2 powder. This brings to a total of 9987gm of TiB2 using a new recipe.

3 Joel has completed leaching of first 4918gm (1-9 S/S) of TiB2 powder produced using a new recipe. Samples have been collected for analysis.

4 A hot press run was conducted using T/A Union Process ball mill powder. The sample was hot pressed at 6500 psi pressure and at 8 degree per minute heating rate. The slow heating rate was used to obtain a CTP curve. Type "C" thermocouple without argon atmosphere was used. A CTP curve was obtained, however, the disk produced had a thickness of 0.465". This is because the die and punches were remachined several times and more powder had squeezed out along the sides of the puch during the run. (.51)

5 A stainless steel container (bucket) experiment was conducted to measure the temperature two inches above and below the container. A 400gm T/A reaction was made in the container. Thermocouples were placed two inches above and below the container. Temperatures were recorded using a strip chart recorder. The results were submitted to Paul Sykes of AEM.

6 At the request of Joel Tenney, 25gm TiB2 reactions were made using Mg powders supplied by Reade Co. These samples had different particle size and shape.

7 Joel has submitted 12 samples for XRD. Shin is to conduct XRD analysis on the first batch of leached TiB2 powder (new recipe) and 25gm powders.

8 A new shipment of POCO XT graphite has been received last Friday.

9 A work order has been placed with GT POD for electrical outlets near hot press area.

10 I was unable to cut the new graphite because the band saw

locking device is not working. We will have to either repair or replace the locking device.

11 We do not have castable bricks and we are running out of SiC plates that we use in the hot press. Because of the high temperature and pressure, the bricks and the plates crack and do not last long. We have to find alternate solutions to this problems.

12 The machine shop in Area II is a mess. People use the machine shop but do not want to clean. Charles, Billy, and I are not responsible for making the mess. We will not clean the place this time. If we use any equipment in the machine shop, we will clean it as has always been. I replaced the fuses for the lathe. Also the Plasma spray booth is in real mess. People use electric bench saw and do not clean.

FUTURE WORK

1 My first priority is to find some solutions to the problems as mentioned in item 11. Order SiC plates and Blocks or replace with Steel blocks. Ordering takes 4 to 8 weeks and we did not consider these items in the budget.

2 Repair or replace the locking device of the band saw.

3 Continue SHS TiB2 reactions to fulfill 50lb of leached powder.

4 Continue hot pressing, set the priority TiB2 or T/A.

Dr. Logan :

polishing of the sintered sample eliminated the SiO_2 content successfully.

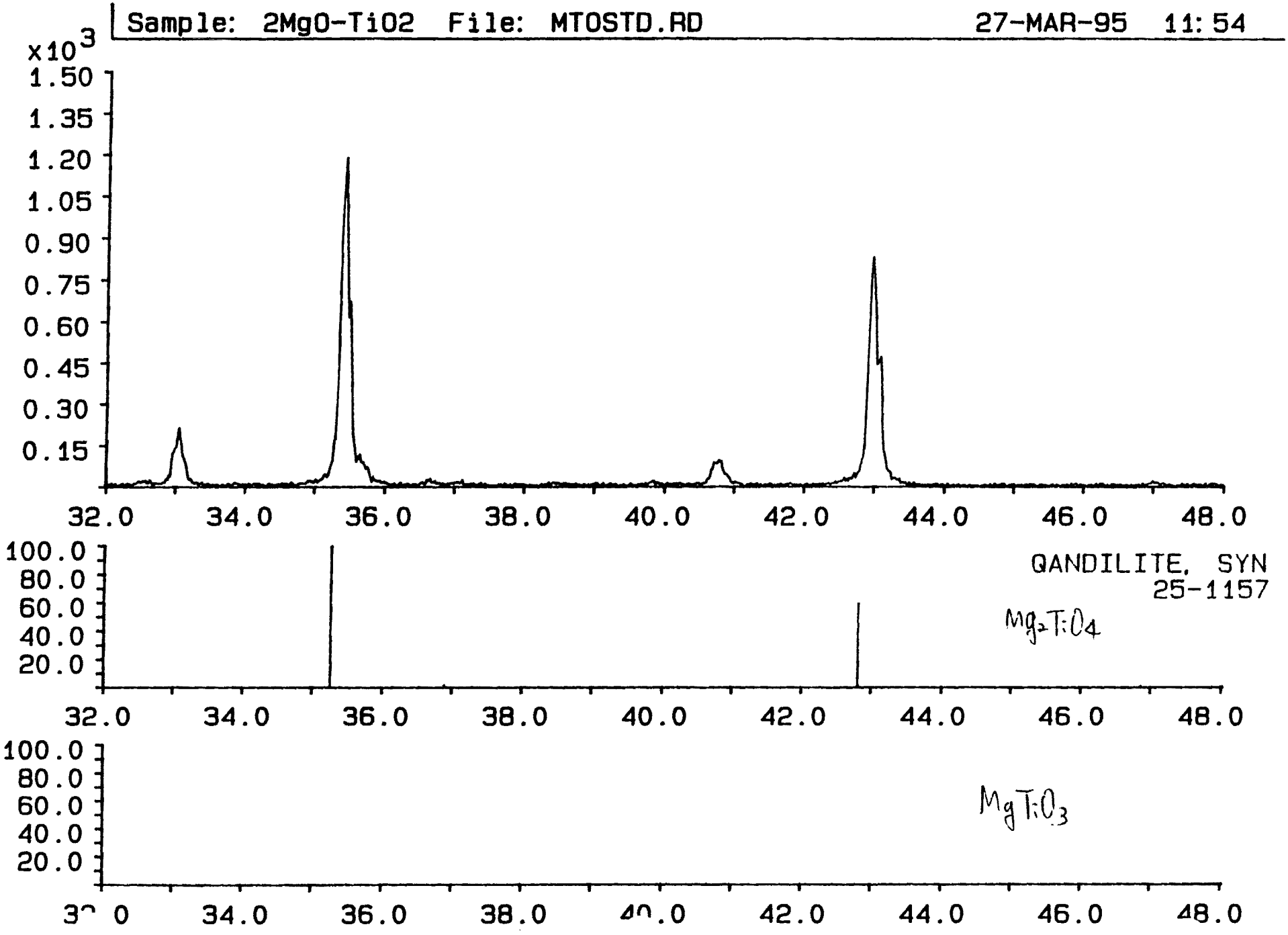
However, the sample also showed $MgTiO_3$ phase, implying the lack of MgO ($MgTiO_3 + MgO \rightarrow Mg_2TiO_4$)

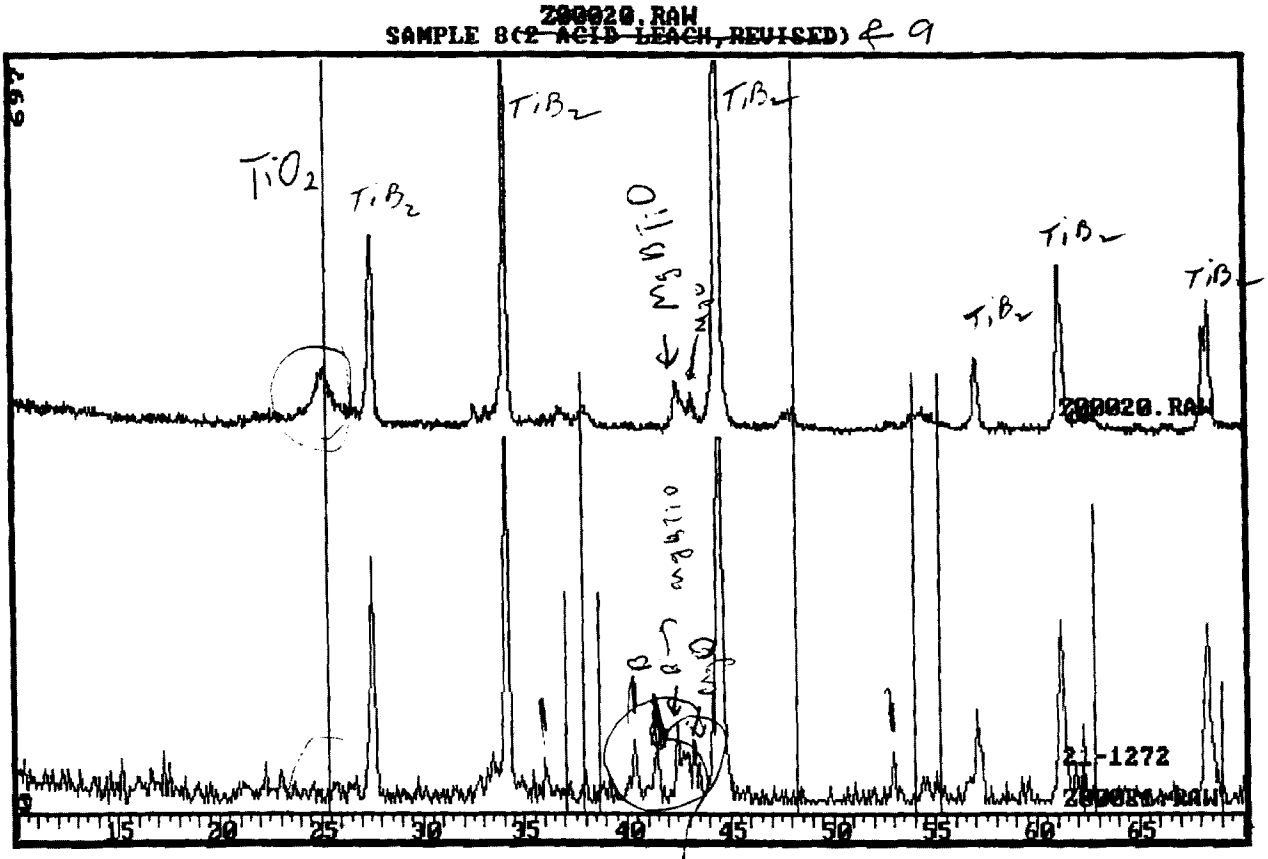
I guess MgO is evaporated at 1610°C. for ~4 hr.

Instead of adding excess amount of MgO for pure Mg_2TiO_4 formation, (it requires furnace runs of 1610°C temperature)

I am assuming this sample 90% Mg_2TiO_4, and then making Calibration Curve today. 3/17/95

— H. Shin.


Sample: 2MgO-TiO2 File: MTOSTD.RD 27-MAR-95 11:54
x10^3
1.50
1.35
1.20
1.05
0.90
0.75
0.60
0.45
0.30
0.15
32.0 34.0 36.0 38.0 40.0 42.0 44.0 46.0 48.0
100.0
80.0
60.0
40.0
20.0
QANDILITE, SYN
25-1157
Mg2TiO4
32.0 34.0 36.0 38.0 40.0 42.0 44.0 46.0 48.0
100.0
80.0
60.0
40.0
20.0
MgTiO3
34.0 36.0 38.0 42.0 44.0 46.0 48.0



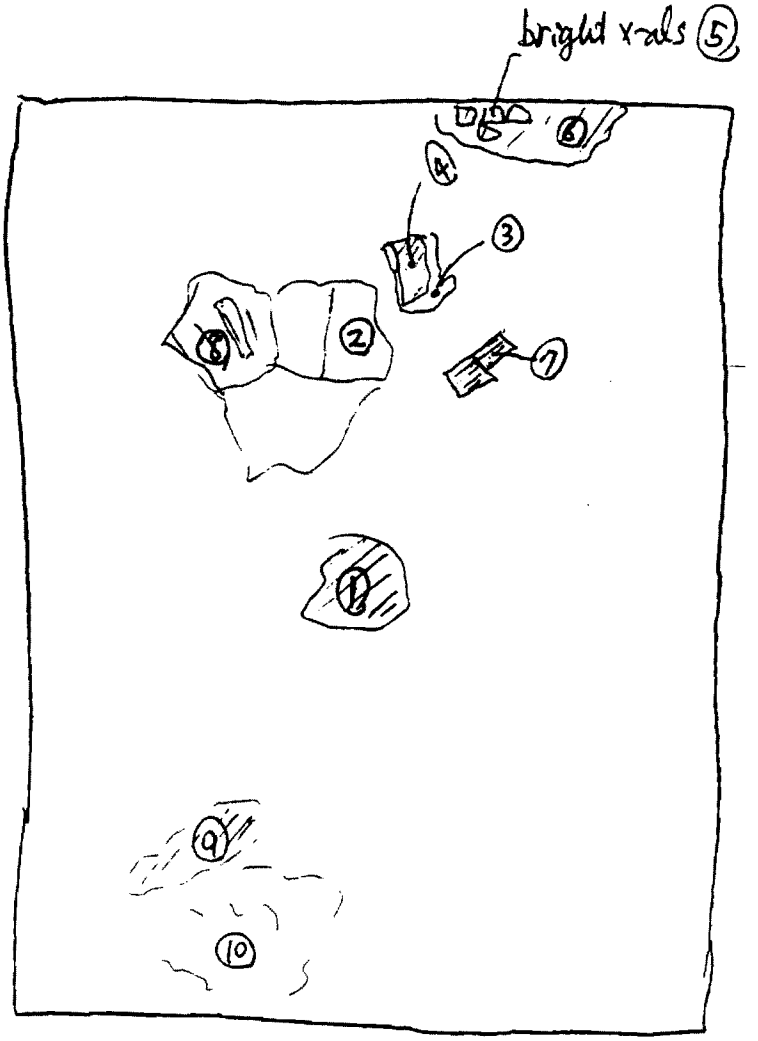
(8)

,2-
.4

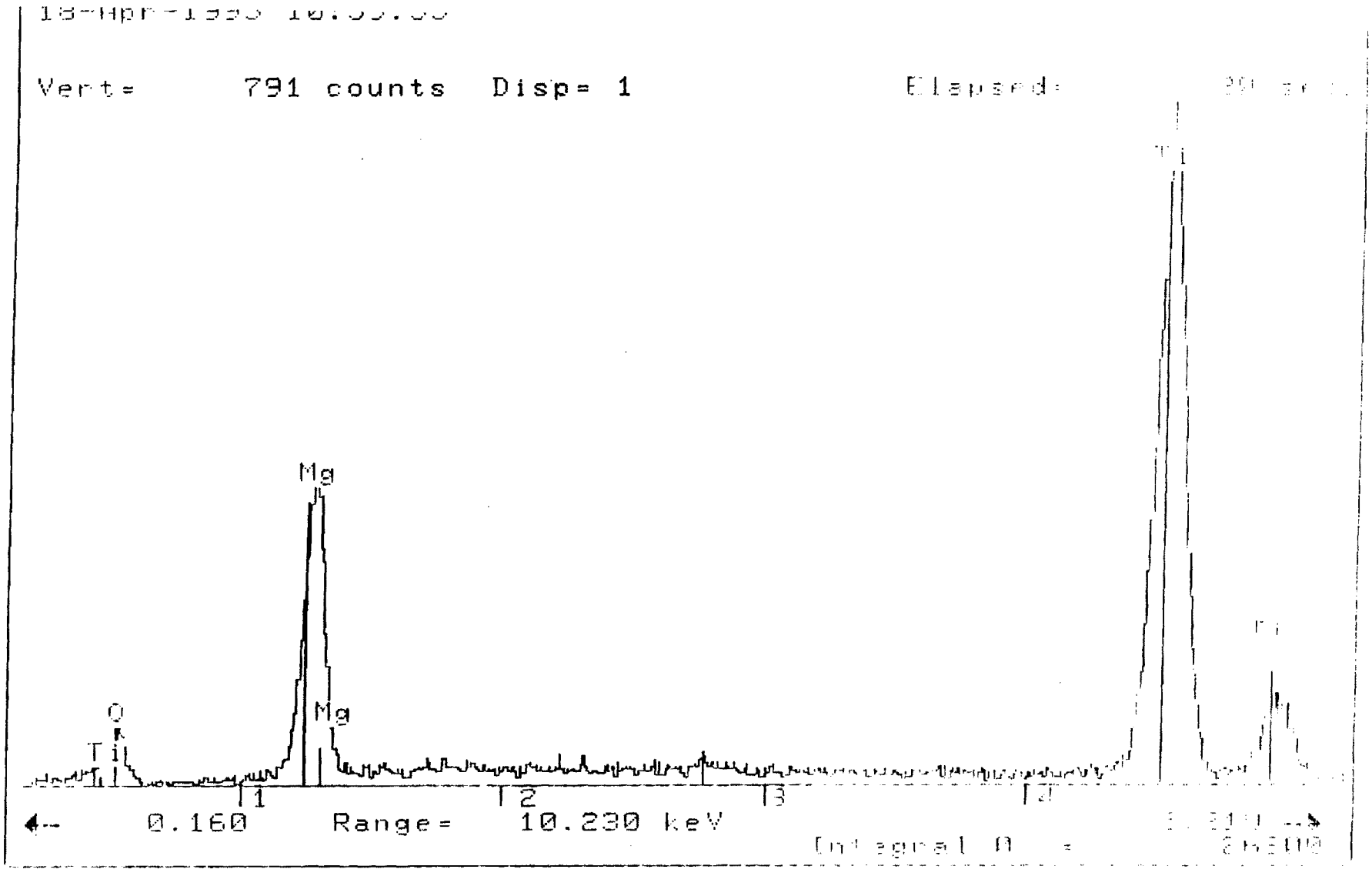
(9)

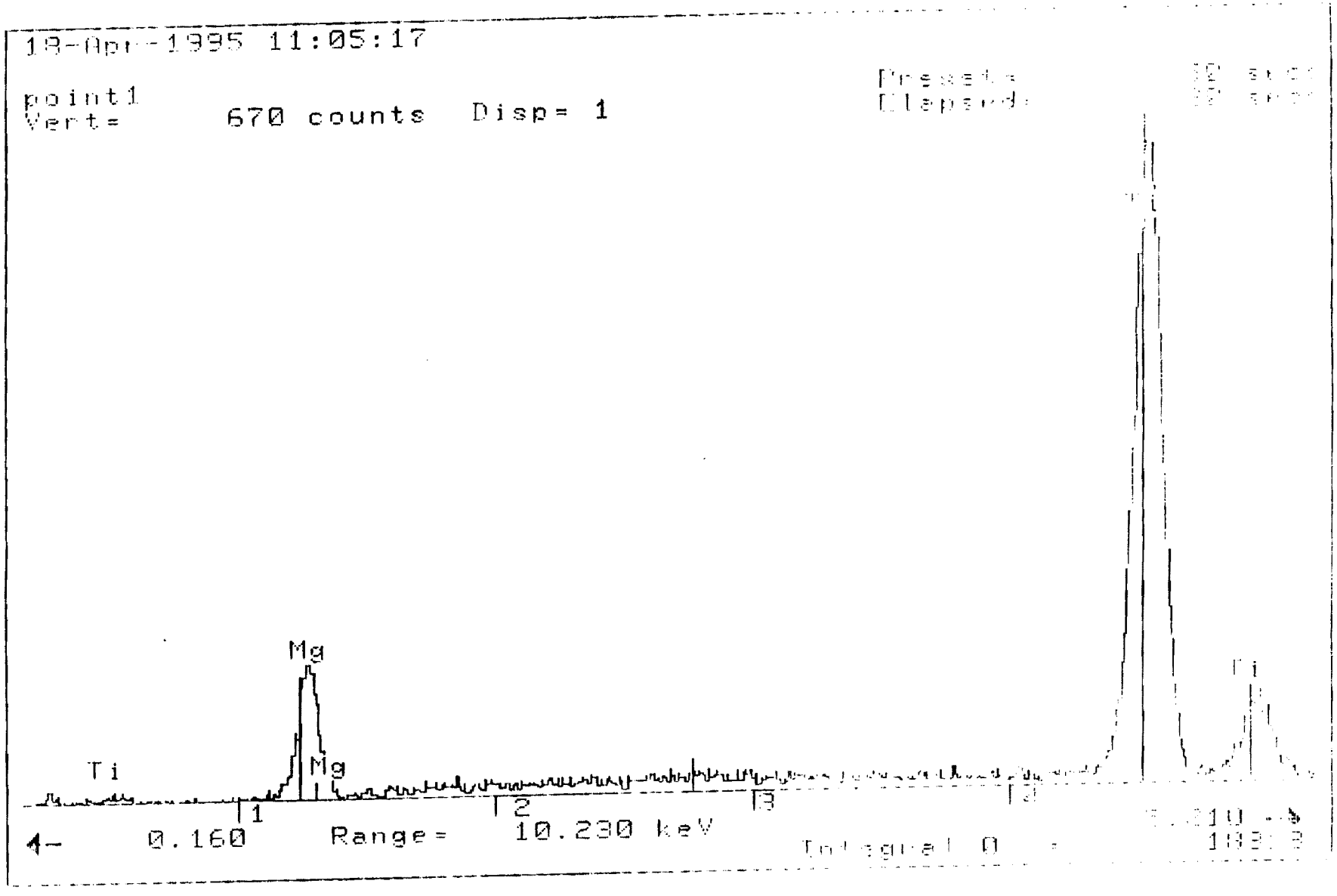
h-3.0
at

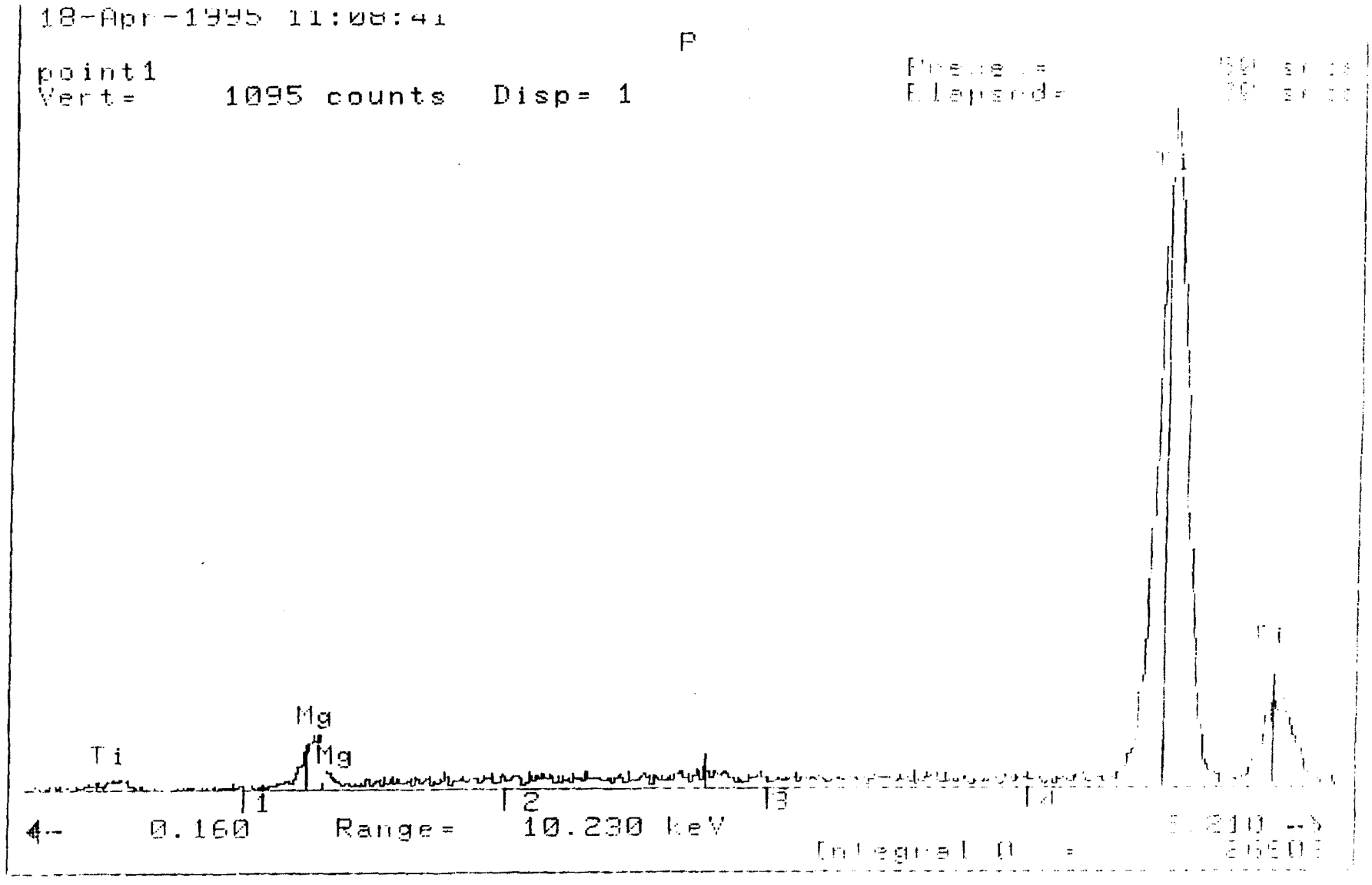
MgO + iron ates
TiO + titan ates

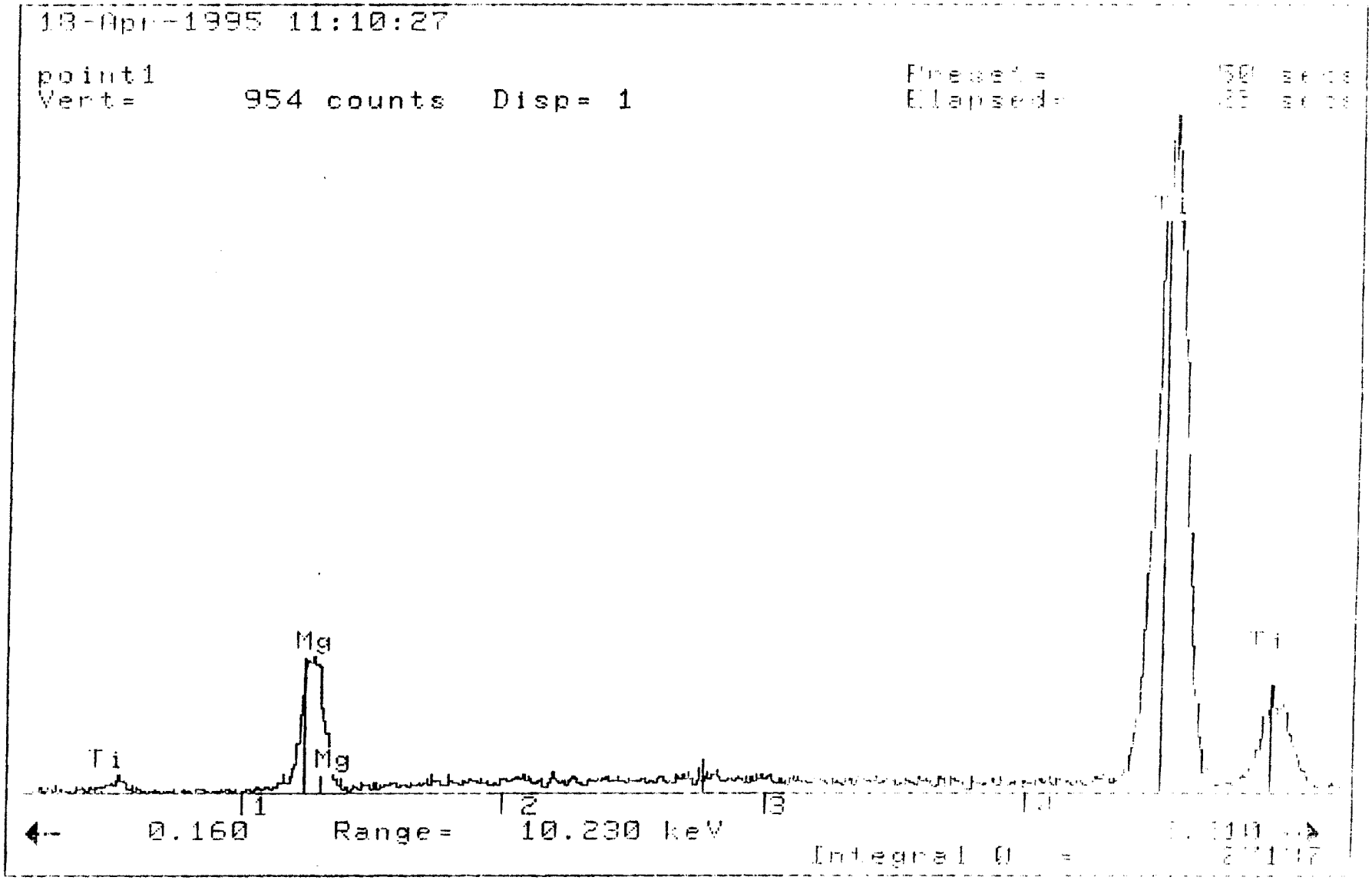


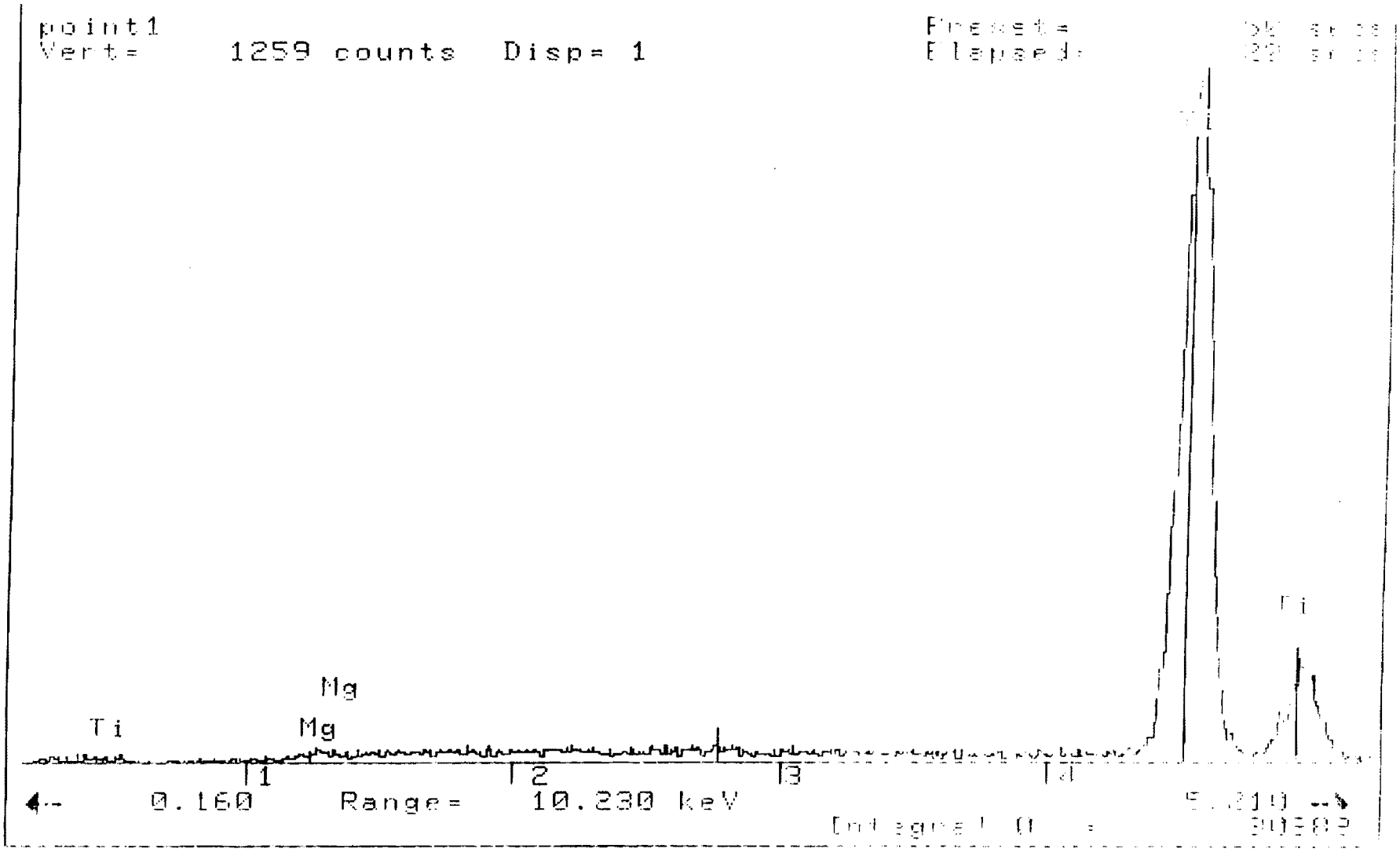
TiB2 Fracture surface

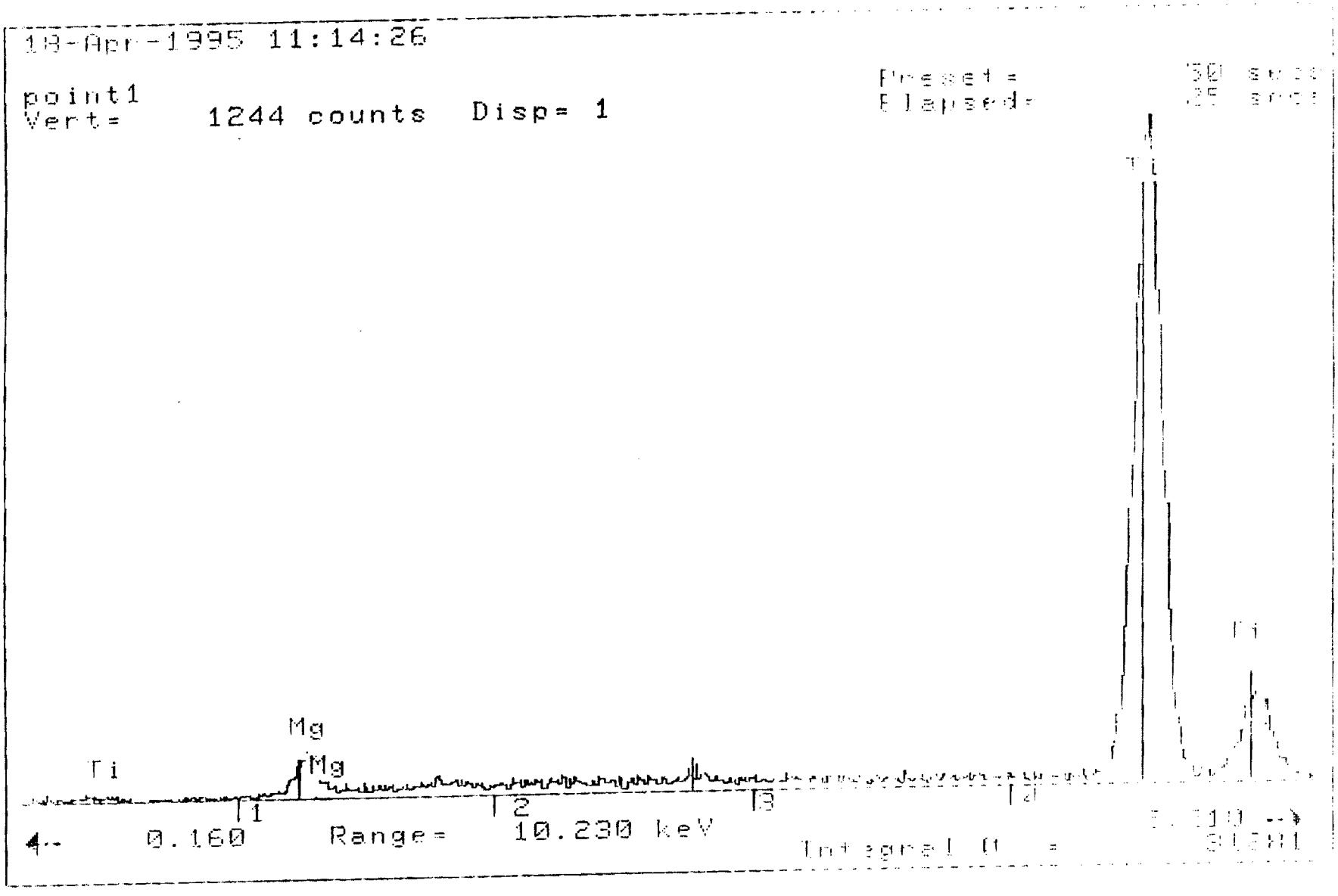

Vert= 791 counts Disp= 1
Elapsed=
Ti
Mg
O
Ti
Mg
Ti
1
2
3
0.160
Range= 10.230 keV

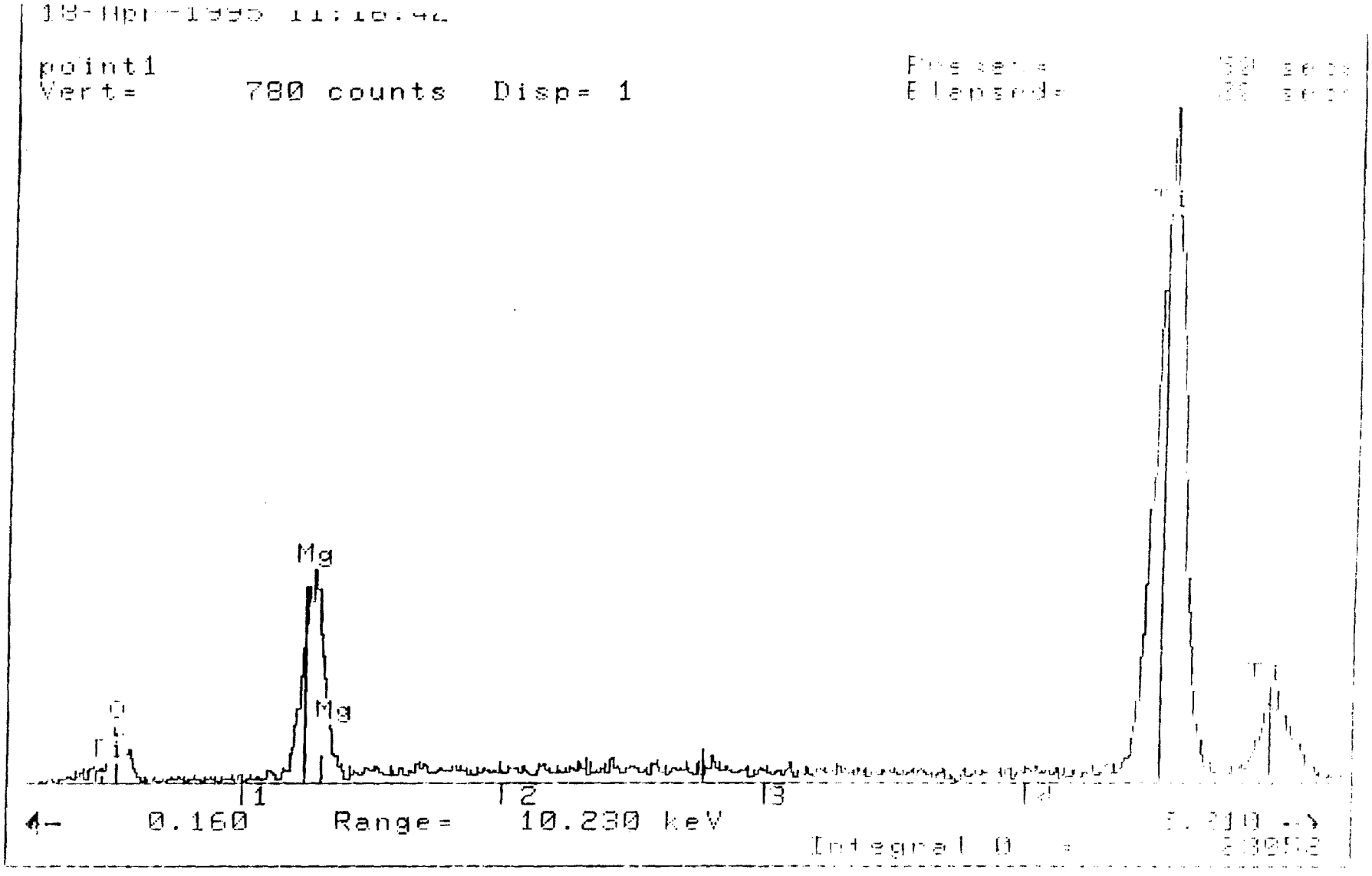

18-Apr-1995 11:05:17
point1
Vert= 670 counts Disp= 1
Mg
Ti
Mg
Ti
1
2
3
0.160
Range= 10.230 keV

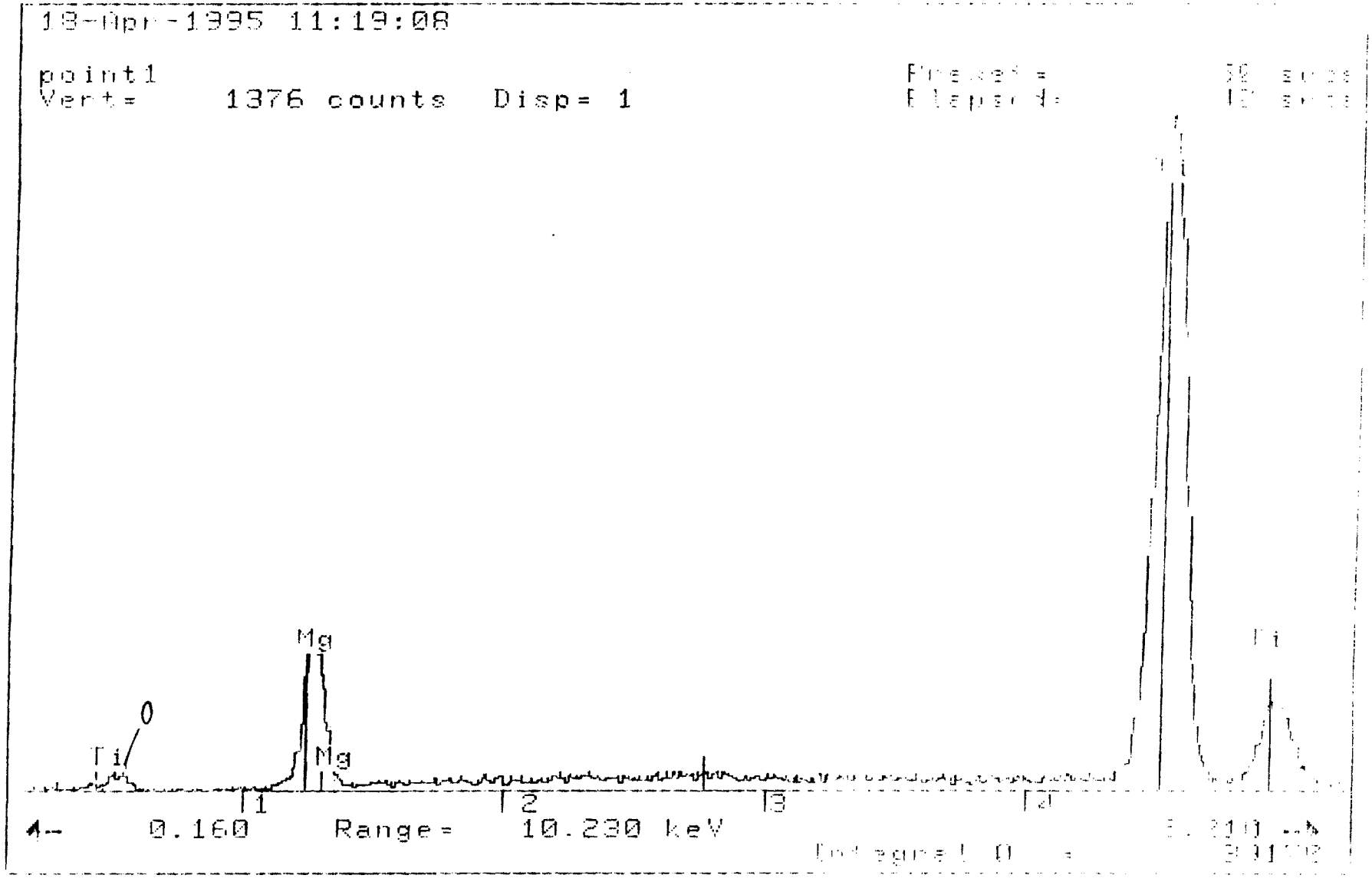

18-Apr-1995 11:08:41
P
point1
Vert= 1095 counts Disp= 1
Ti
Mg
Mg
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV

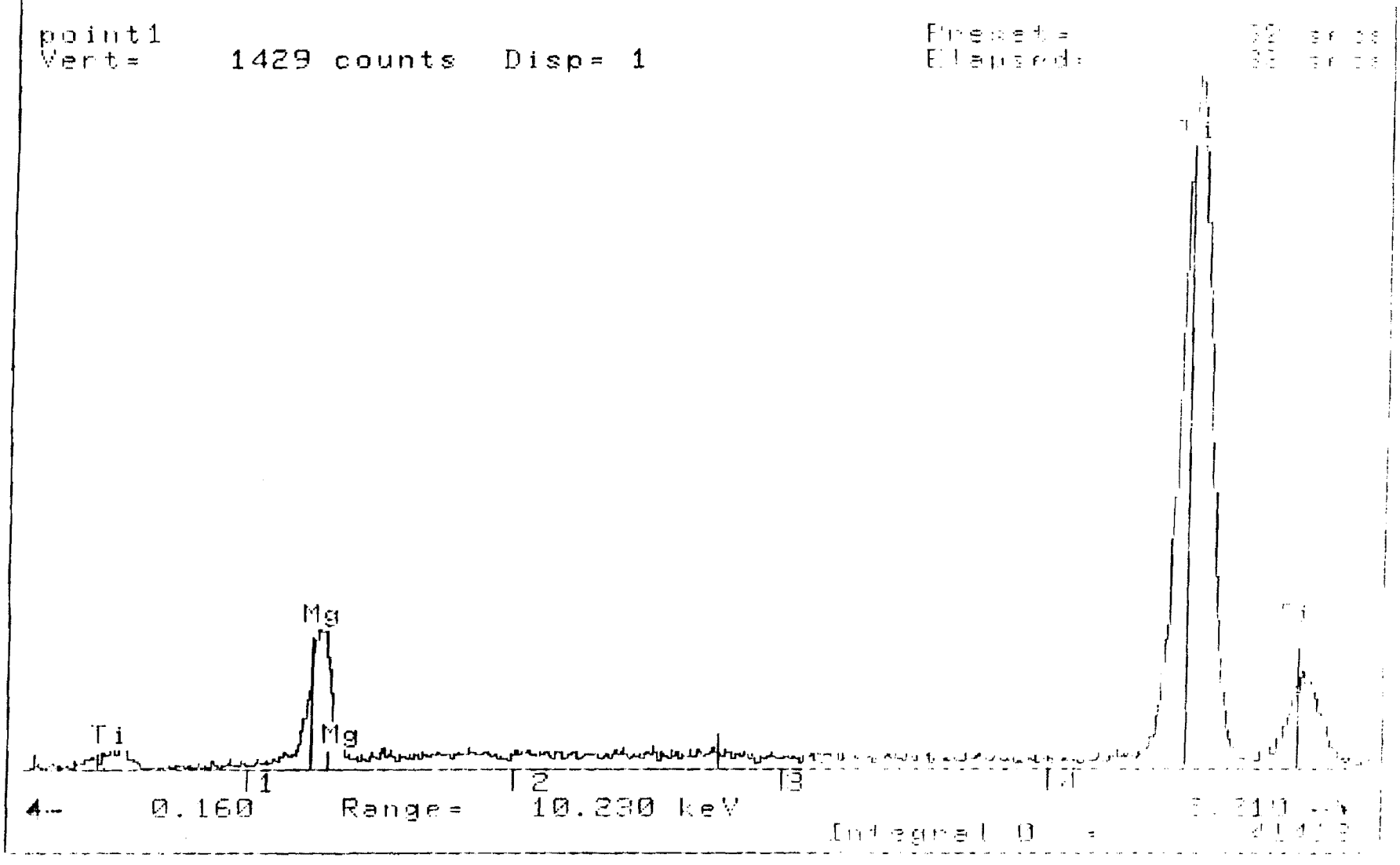

13-Apr-1995 11:10:27
point1
Vert= 954 counts Disp= 1
Preset=
Elapsed=
Ti
Mg
Ti
Ti
Mg
1
2
3
0.160
Range= 10.230 keV
Integral 0 =

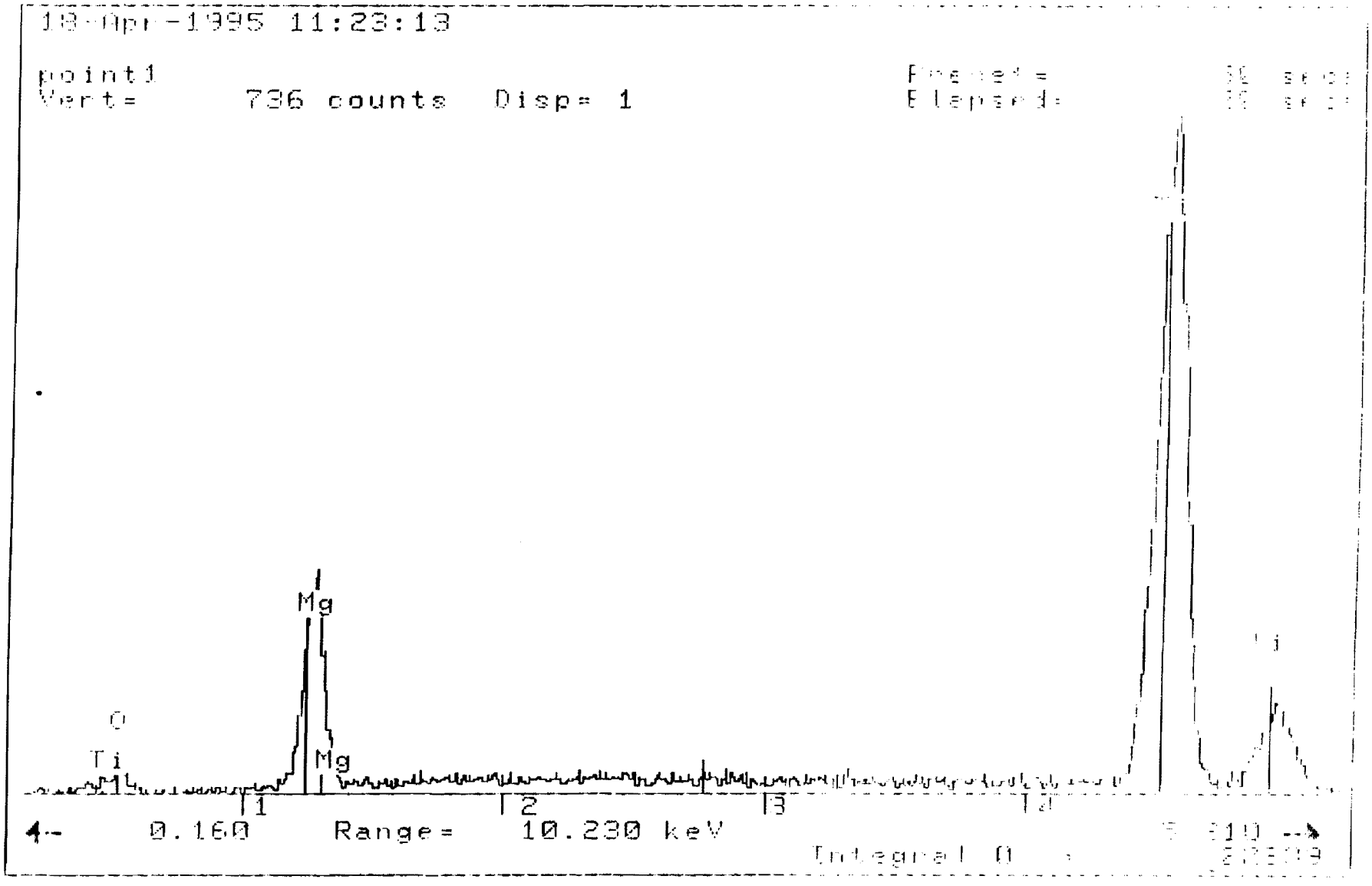

point1
Vert= 1259 counts Disp= 1
Preset=
Elapsed:
Ti
Mg
Ti
Mg
1
2
3
4
0.160
Range= 10.230 keV


18-Apr-1995 11:14:26
point1
Vert= 1244 counts Disp= 1
Preset=
Elapsed=
Ti
Ti
Mg
Mg
1
2
3
4
0.160
Range= 10.230 keV


point1
Vert= 780 counts Disp= 1
Mg
Mg
Ti
Ti
Ti
1
2
3
0.160
Range= 10.230 keV


18-Apr-1995 11:19:08
point1
Vert= 1376 counts Disp= 1
Mg
O
Ti
Mg
Ti
1
2
3
4
0.160
Range= 10.230 keV


point1
Vert= 1429 counts Disp= 1
Mg
Ti
Mg
Ti
1
2
3
4
0.160
Range= 10.230 keV


18-Apr-1995 11:23:13
point1
Vert= 736 counts Disp= 1
Mg
O
Ti
Mg
Ti
1
2
3
4
4- 0.160 Range= 10.230 keV

COPY For Dr. Logan

second

Surface Characterization of TiB_2 Electrode Materials Using Analytical Scanning Electron Microscopy

By Hyunho Shin

March 9, 1995

I. Experimental Procedure

The electrode material was immersed into a chryolite (sodium fluoride and aluminum melt) as a cathode at 1000°C in an inert atmosphere. The top end of the TiB_2 electrode was supported by a refractory ceiling using molybdenum and calcium silicate cement material.

The end portion of the sample rod (about 3 mm from immersed end) was cut using a high speed diamond saw. After cleaning (using an ultrasonic cleaner), drying, the cut surface was coated with gold via vacuum sputtering for scanning electron microscopy (SEM) analysis.

II. Results and Discussion.

Figure 1 shows a representative cross sectional view of the TiB_2 rod. Relatively clear melt/TiB_2 interface is observed. While morphology of the surface is apparent in Figure 1, chemical contrast is unclear due to the secondary electron mode.

For a more clear chemical contrast, backscattered mode of the same area is shown in Figure 2. In a back scattered mode, areas with high atomic number elements show up in bright color while vice versa for the area of low atomic number elements. From this viewpoint, 9 areas of interest were selected as sketched in Figure 3.

Figures 4 - 13 show EDS spectra obtained from areas 1 - 9, respectively. The very bright area (areas 1 and 2) shows up to be rich in molybdenum. Hence the use of molybdenum as supporting material should be avoided.

The relatively dark area surrounding the TiB_2 electrode (area 3) is shown to be rich in aluminum.

The area 4 (surrounded by aluminum rich area) is brighter than its surroundings. This means it contains higher atomic elements than its aluminum-rich surroundings. This area is shown to be rich in titanium

and aluminum implying the possibility of titanium aluminide formation.

The area 5 contains very bright spots (molybdenum). This area is rich in silicon, aluminum, molybdenum, sodium and titanium. Note that presence of titanium is quite appreciable comparing to is distance from TiB_2 surface. The presence of silicon indicates that the calcium silicate cement is not an adequate material for TiB_2 application as an electrode.

The area 6 is darker than its surrounding. This area should contain light elements. However molybdenum was detected. This was probably because the electron beam was positioned its neighboring bright areas (The EDS signal is obtained in an secondary electron mode as shown in Figure 1. In Figure 1, the area 6 is hard to find for EDS analysis.)

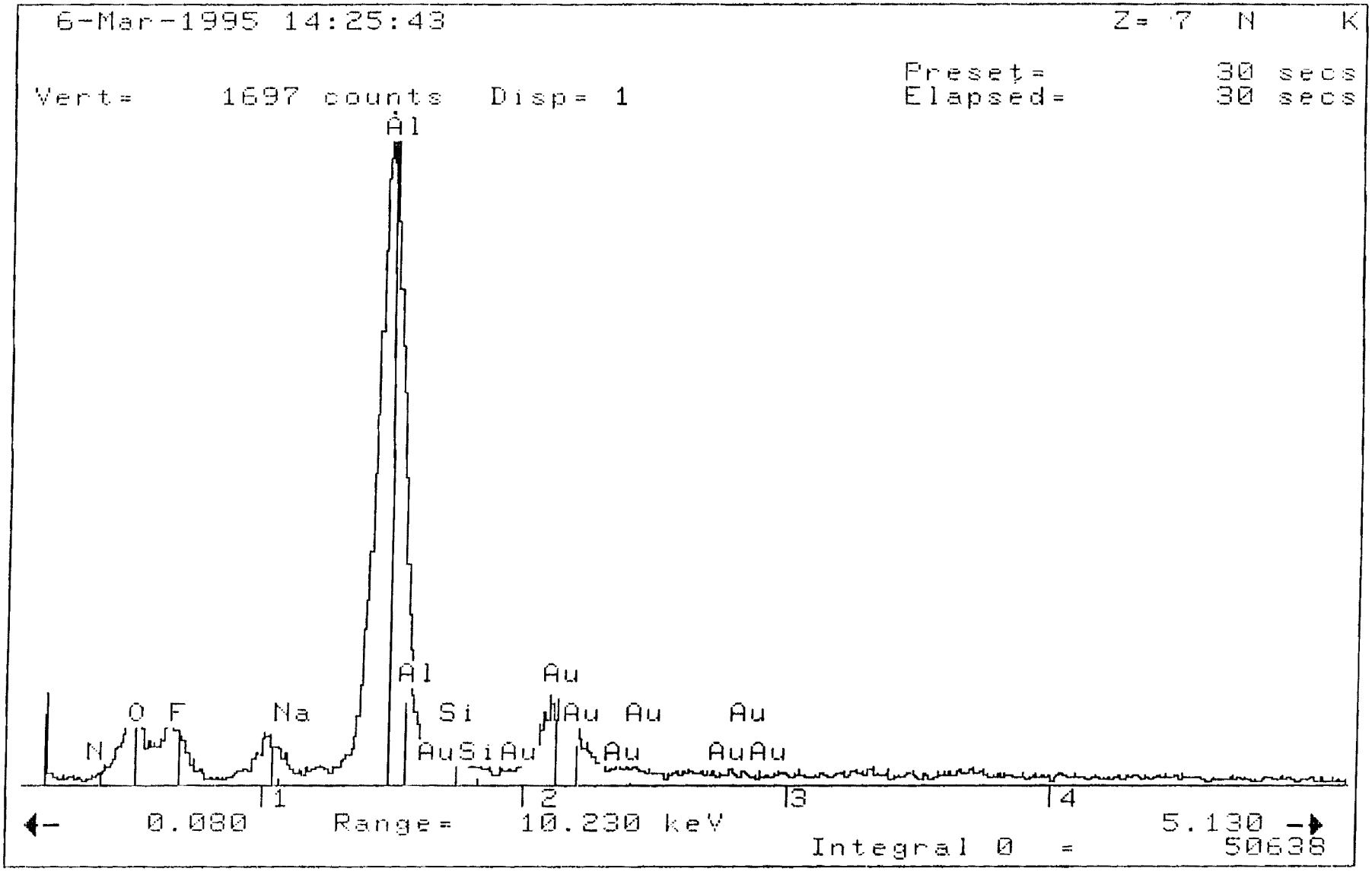
The areas 7-9 is the bulk of TiB_2 electrode. They do not show any appreciable difference in T-rich EDS spectra.

Figure 1

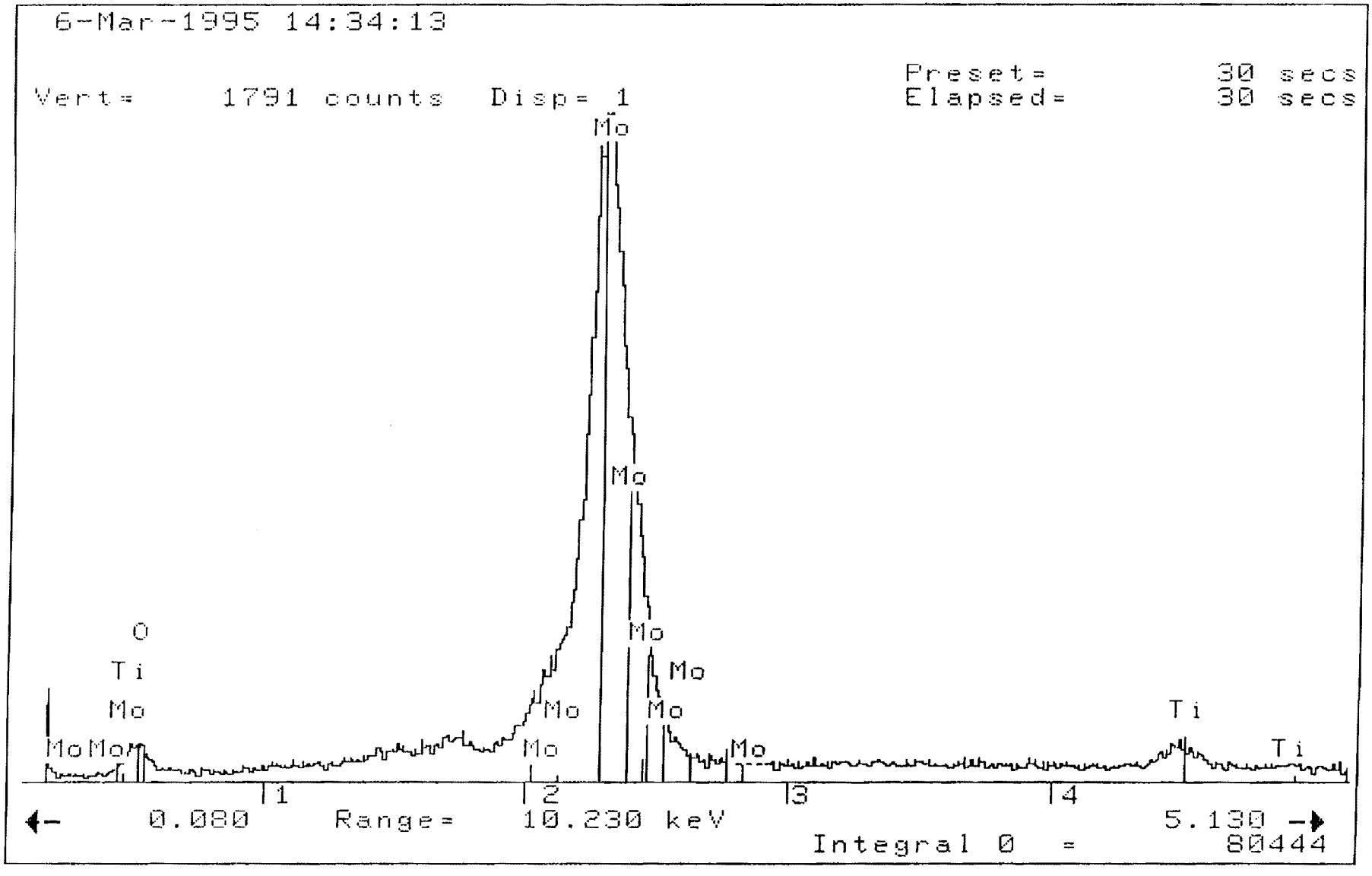
Serrata

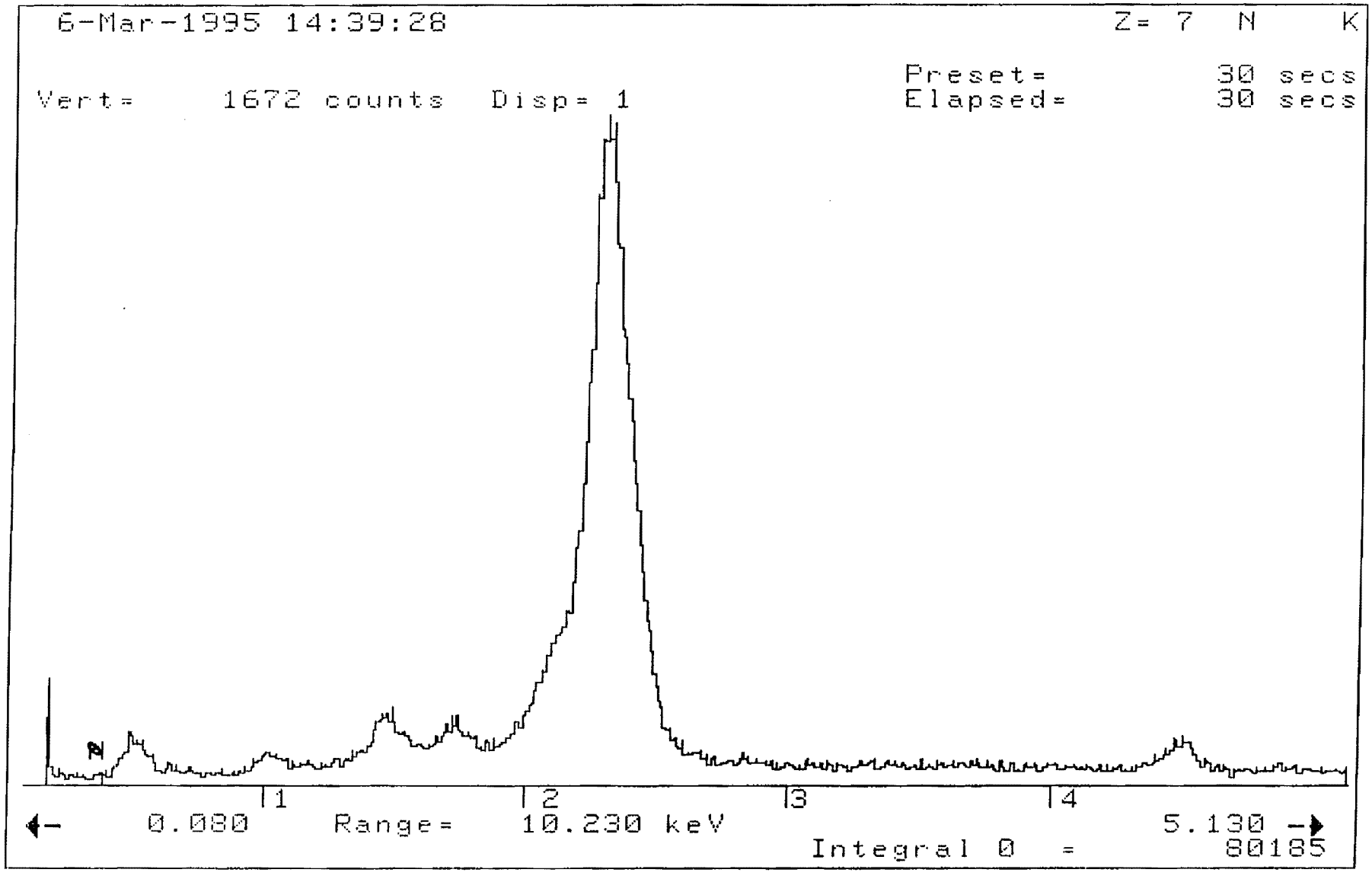
Figure 2

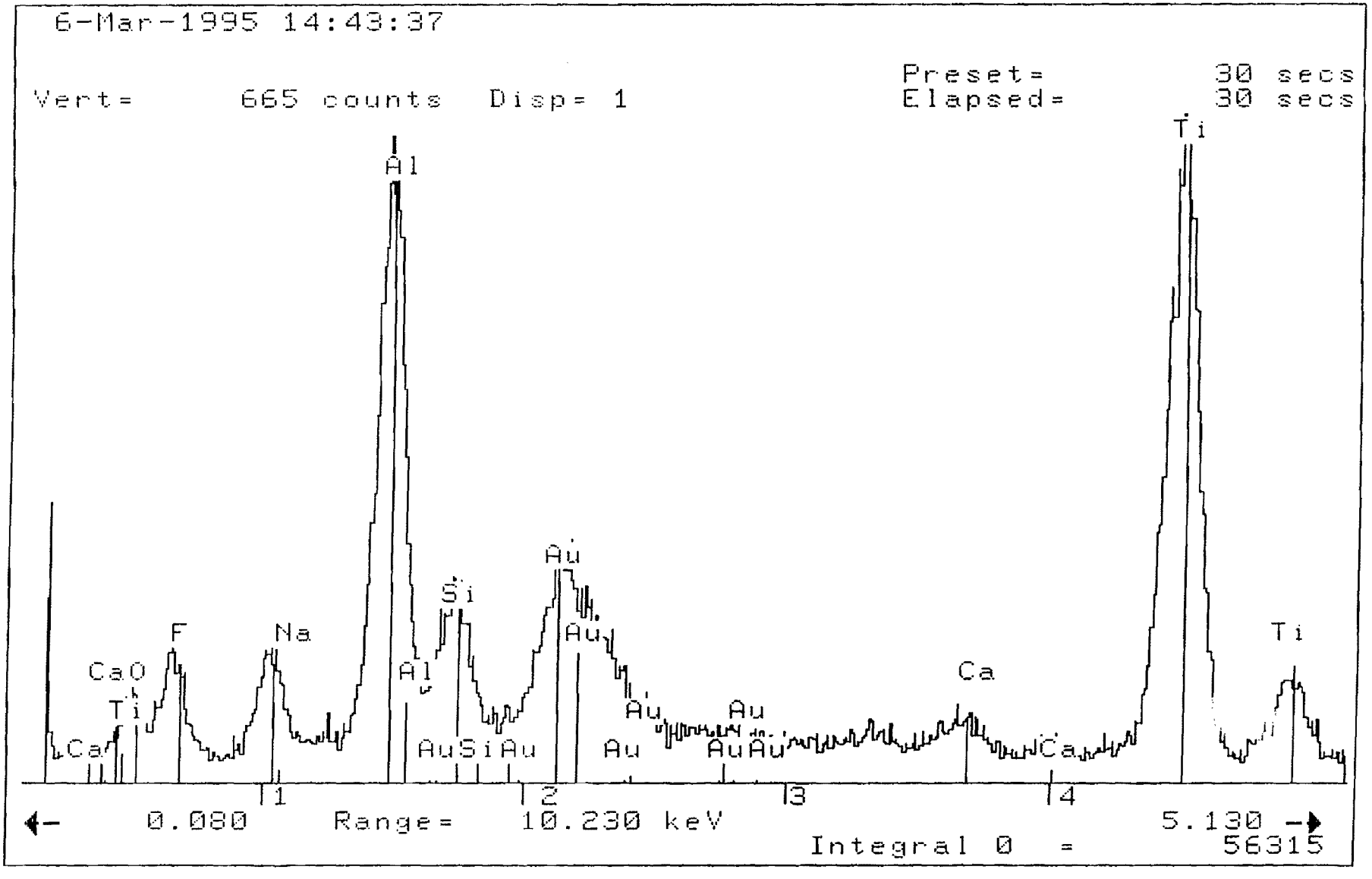
Figure 3

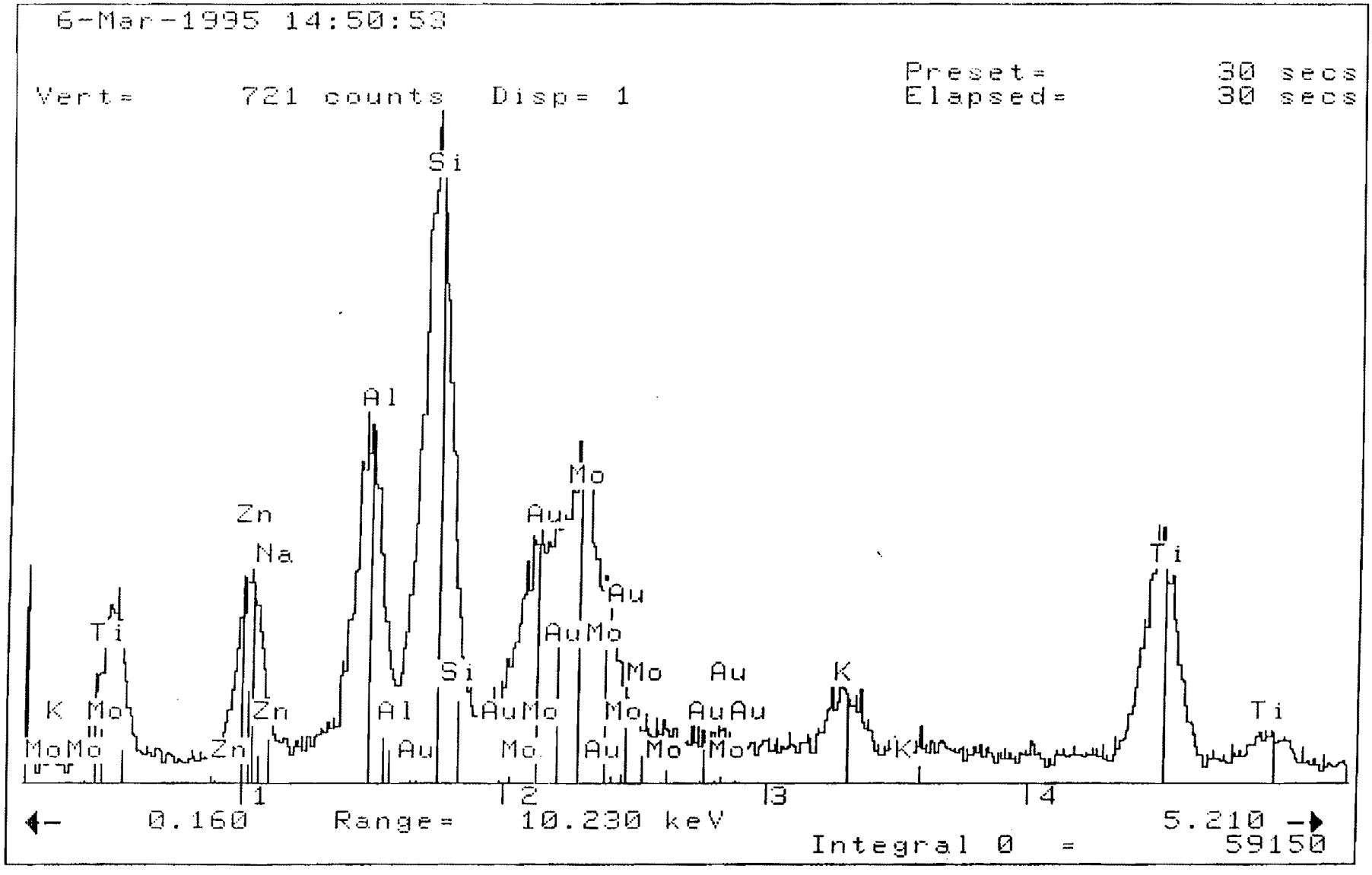

6-Mar-1995 14:25:43
Z= 7 N K
Preset= 30 secs
Vert= 1697 counts Disp= 1
Elapsed= 30 secs
Al
Al
Au
O F
Na
Si
Au Au Au
N
Au Si Au
Au
Au Au
1
2
3
4
0.080
Range= 10.230 keV
5.130
Integral 0 = 50638

A .2

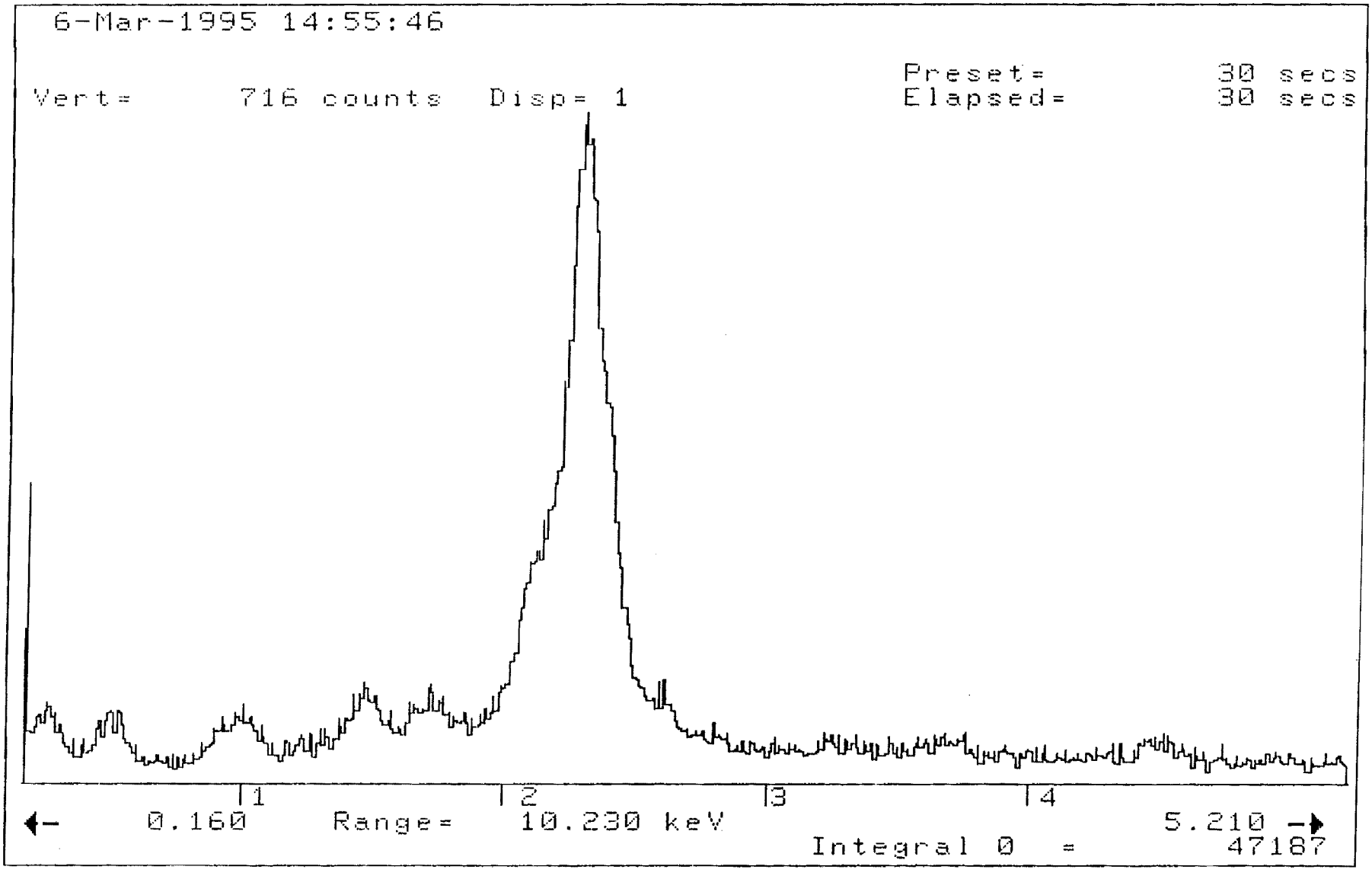

6-Mar-1995 14:34:13
Vert= 1791 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
O
Ti
Mo
Mo Mo
Mo
Mo
Mo
Mo
Mo
Mo
Mo
Ti
Ti
1
2
3
4
0.080
Range= 10.230 keV
5.130
Integral 0 = 80444

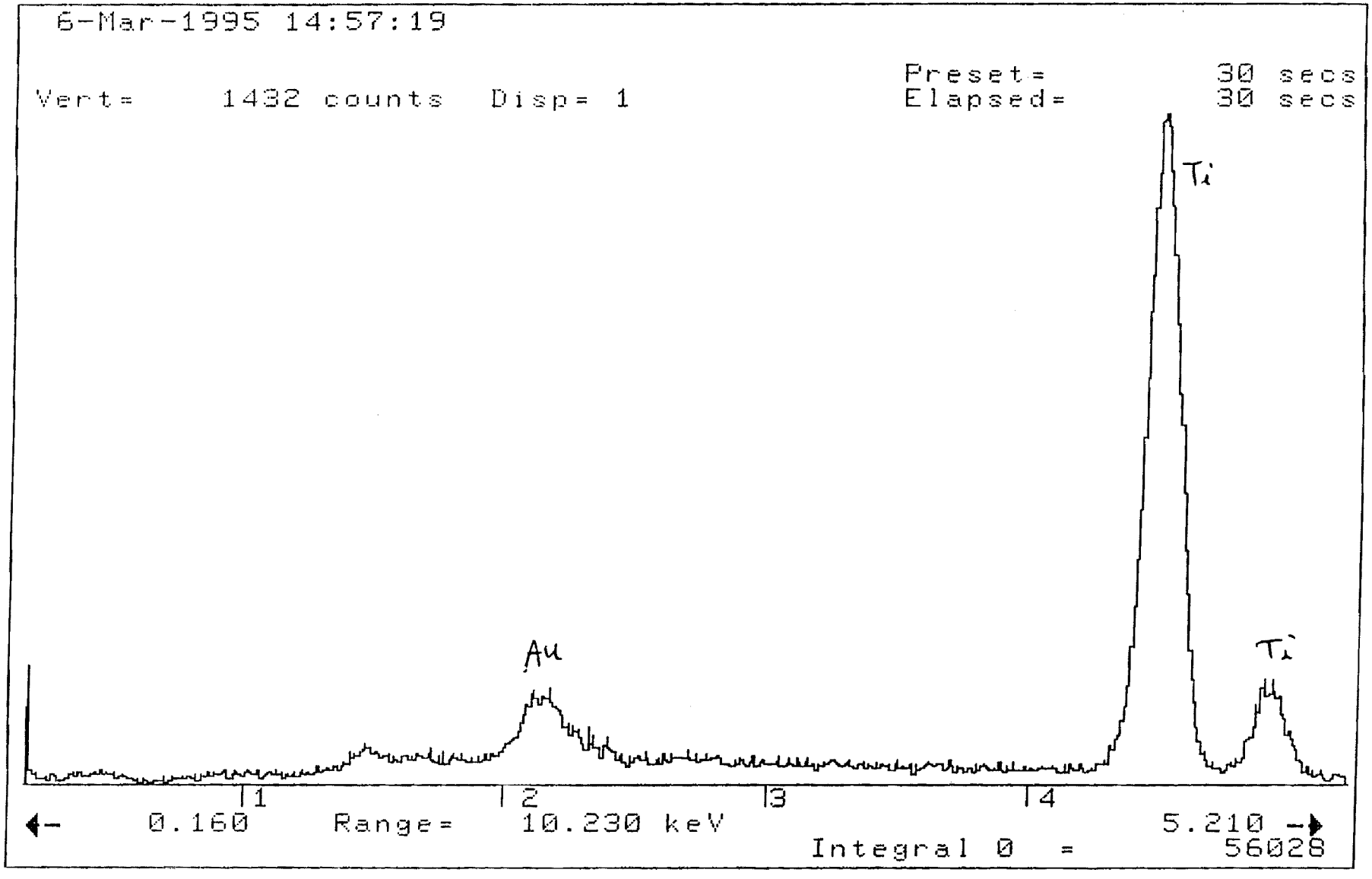

6-Mar-1995 14:39:28
Z= 7 N K
Preset= 30 secs
Elapsed= 30 secs
Vert= 1672 counts Disp= 1
N
1
2
3
4
0.080
Range= 10.230 keV
5.130
Integral 0 = 80185

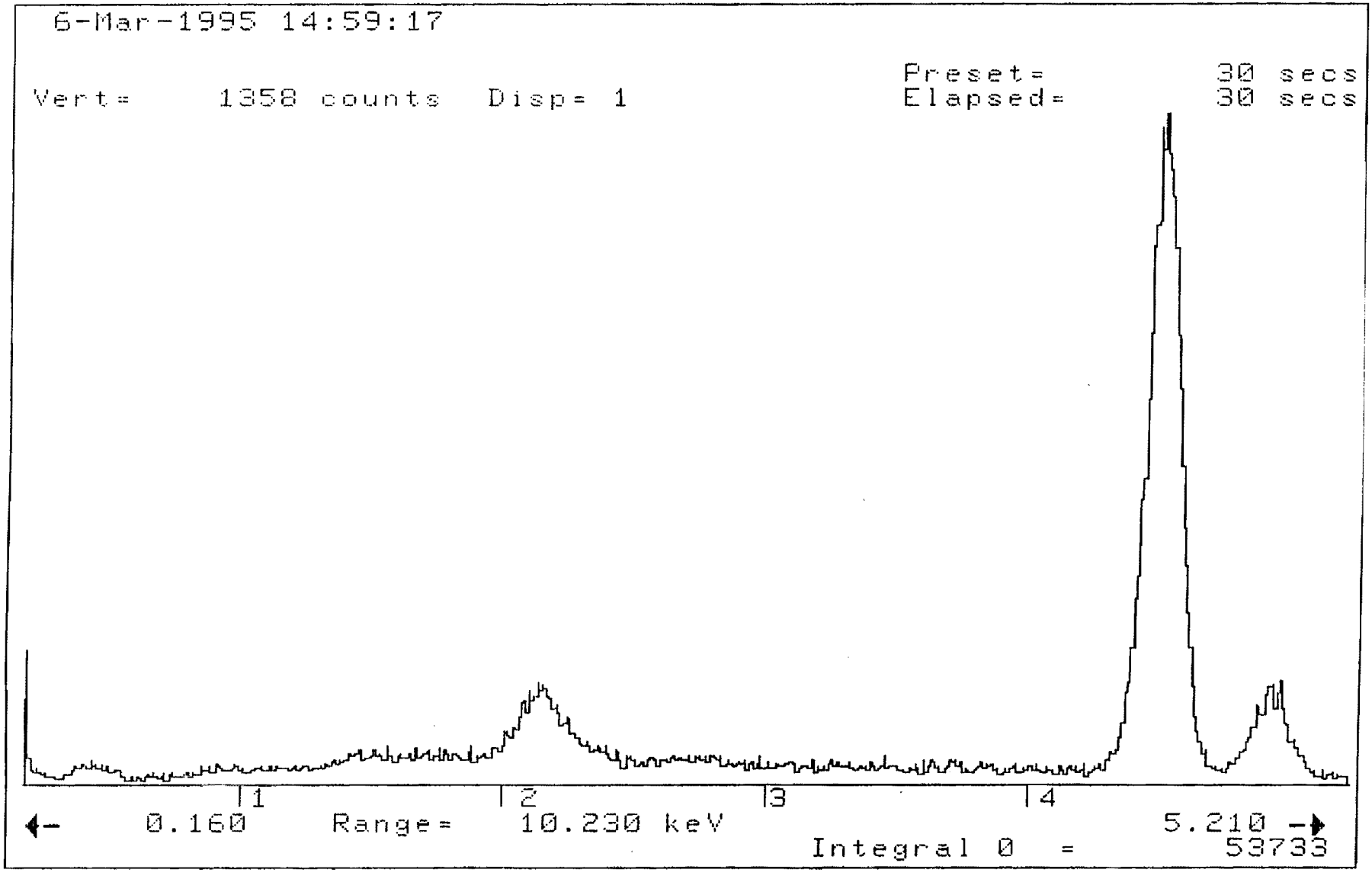

6-Mar-1995 14:43:37
Vert= 665 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
Al
Ti
Si
Au
F
Na
Ca
O
Ti
Ca
Al
Au
Si
Au
Au
Au
Au
Au
Au
Ca
Ca
Ti
1
2
3
4
0.080
Range= 10.230 keV
5.130
Integral 0 = 56315

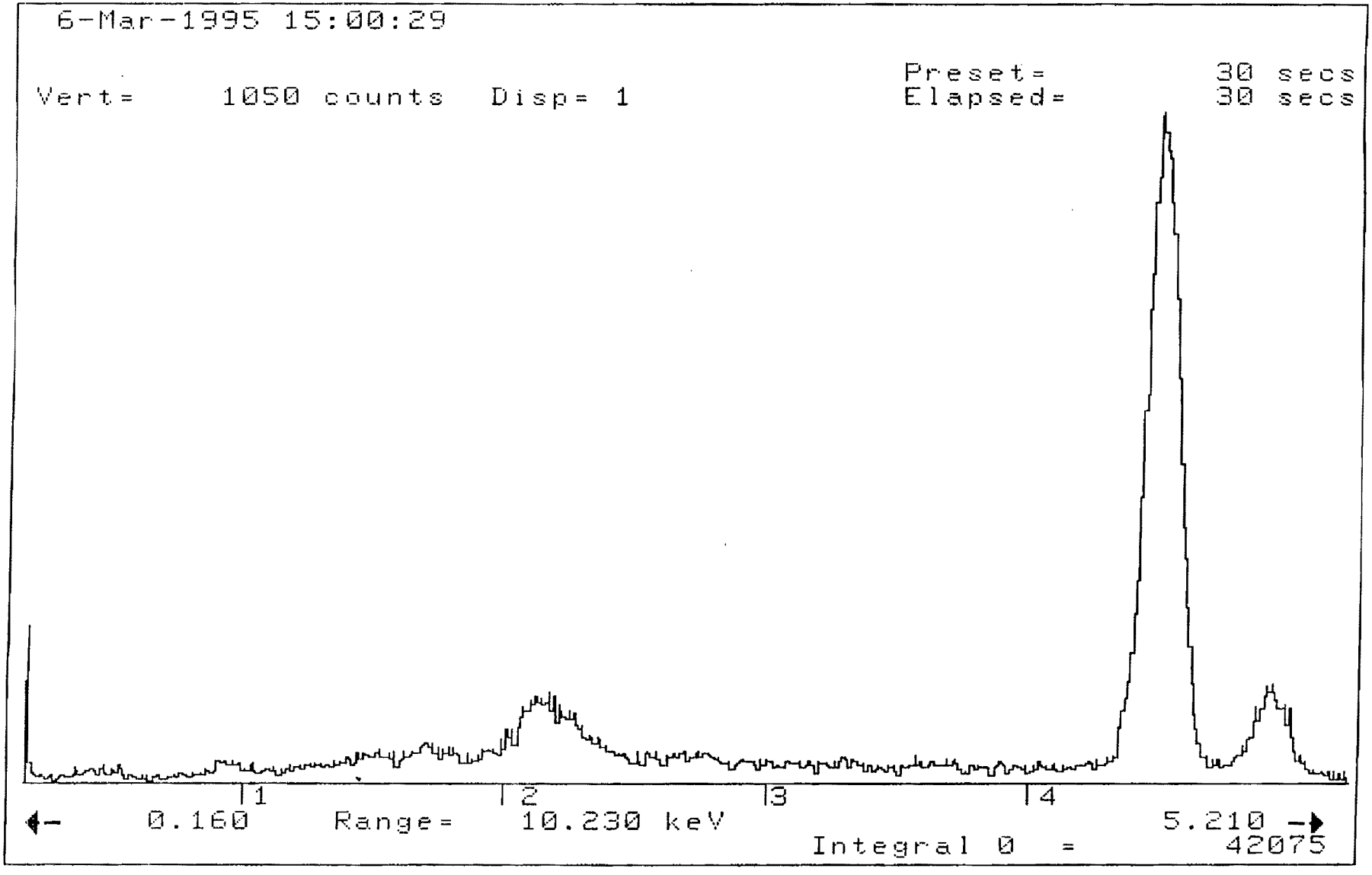

6-Mar-1995 14:50:53
Vert= 721 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
Si
Al
Zn
Na
Mo
Au
Ti
K
Mo
Mo
Zn
Zn
Al
Au
Si
Au
Mo
Mo
Au
Mo
Mo
Au
Au
Mo
Au
Au
K
K
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 59150

Area 0


6-Mar-1995 14:55:46
Vert= 716 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 47187


6-Mar-1995 14:57:19
Vert= 1432 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
Ti
Au
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 56028


6-Mar-1995 14:59:17
Vert= 1358 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 53733


6-Mar-1995 15:00:29
Vert= 1050 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 42075

Polished Surface Characterization of the Second TiB_2 Electrode at High Magnification

March 21, 1995

By Hyunho Shin

I. Introduction

The fracture surface molphology provides the nature of surface scales. There has been an evidence of titanium diffusion into the chryolite melt. The high magnification investigation could not release TiB_2/chryolite interfacial characteristics. Hence it is advised to polish the sample and then characterize it.

II. Experimental Procedure

The sample was mounted in an epoxy followed by curing (2 hrs). Sample was polished using a diamond wheel, SiC papers, and then diamond paste (down to submicron size). It took about 2.5 hrs. The sample was then coated with Au in a vacuum sputtering chamber (1 hr). Characterization took about 3.5 hrs.

III. Results

Figure 1 shows a schematic sketch, a secondary electron mode, and a back scattered electron mode of a representative microstructure. In order to take a look at the interfacial microstructure, the faceted (marked as 2) and penninsular (marked as 1) areas are shown in Figure 2. The evidence of chryolite/TiB_2 interaction was not so obvious except that the interface was ragged. Following EDS spoectra
are from areas marked in the sketch in Figure 1. The penninsular area (marked as 1) is rich in titanium, implying TiB_2. The trace aluminum would be due to interaction volume with cyryolite or diffused aluminum from the chryolite. The faceted area (marked as 2) shows a similar result except higher oxygen concentration. The area marked as 3 is shown to be rich in Al, Na, Si, and F, implying chryolite. The circular area (marked as 4) is shown to be rich in titanium and aluminum. The back scattered image in Figure 1 shows that there are many titanium rich islands in chryolite sea. From this, TiB_2
is speculated to loose its titanium content to chryolite.

Figure 3 shows another interfacial area with backscattered mode.
Very similar microstructure as Figure 1 is observed.

Figure 4 shows a sketch, a back scattered mode of an interfacial area, and a magnified backscattered mode of the other interfacial area.
The enlarged back scattered image shows clearly that TiB_2 electrode is unstable in chryolite. The following EDS spectra was taken from areas shown in Figure 4. Areas A and D are rich in titanium. Titanium is apparent even in chryolite area (areas B and G). Areas C and F are shown to be epoxy. Area E looks like a titanium aluminide phase (Ti3Al, TiAl, etc.).

Figure 1

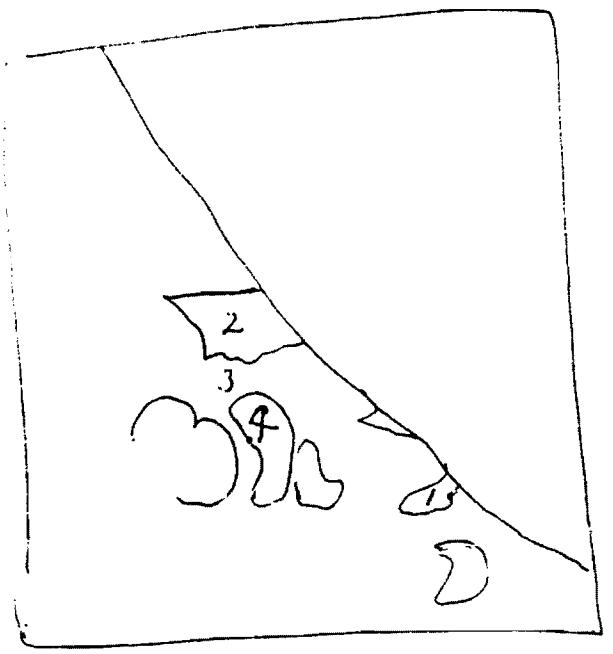


Figure 2

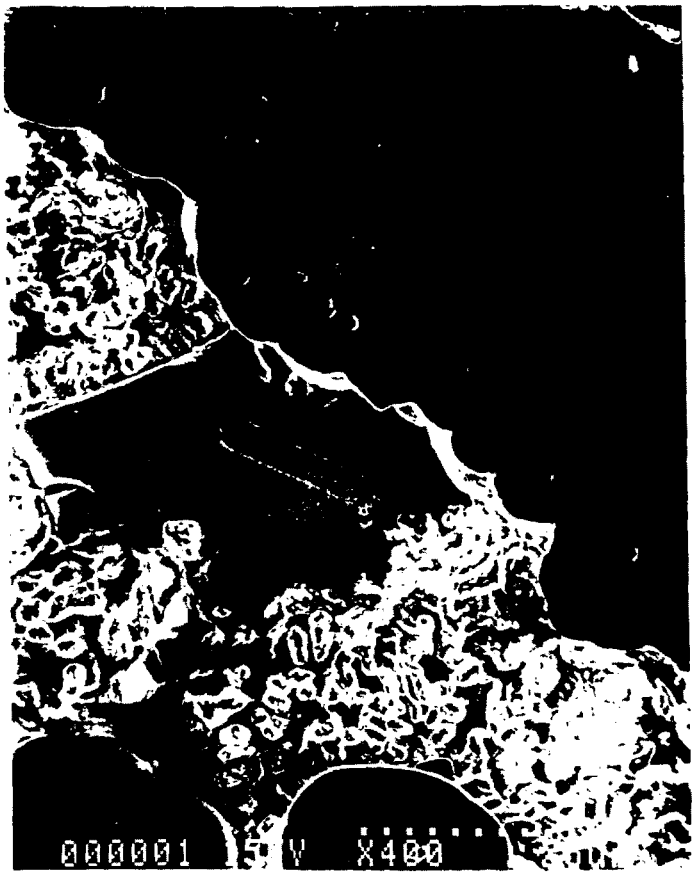


Figure 3

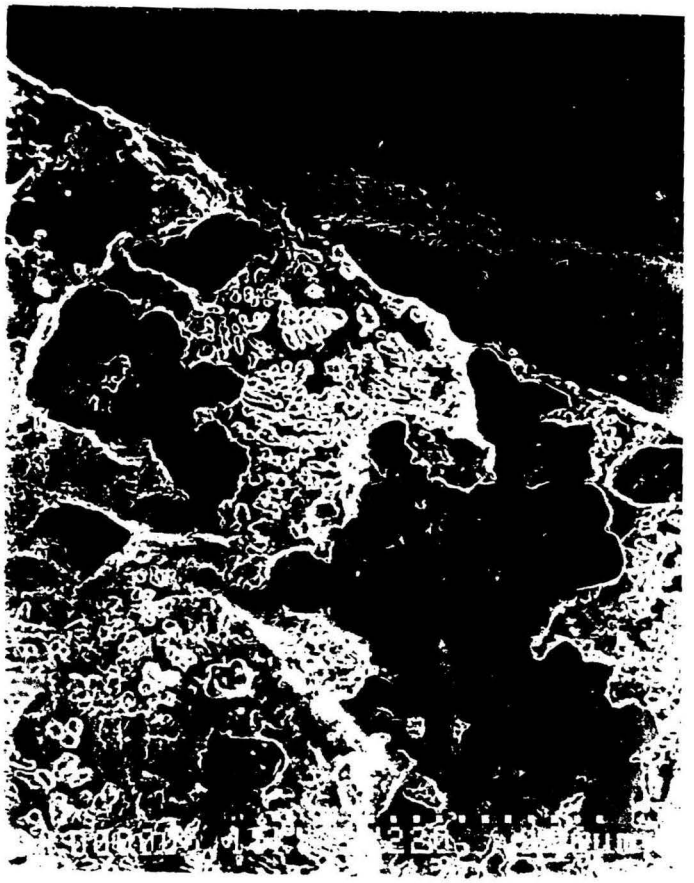
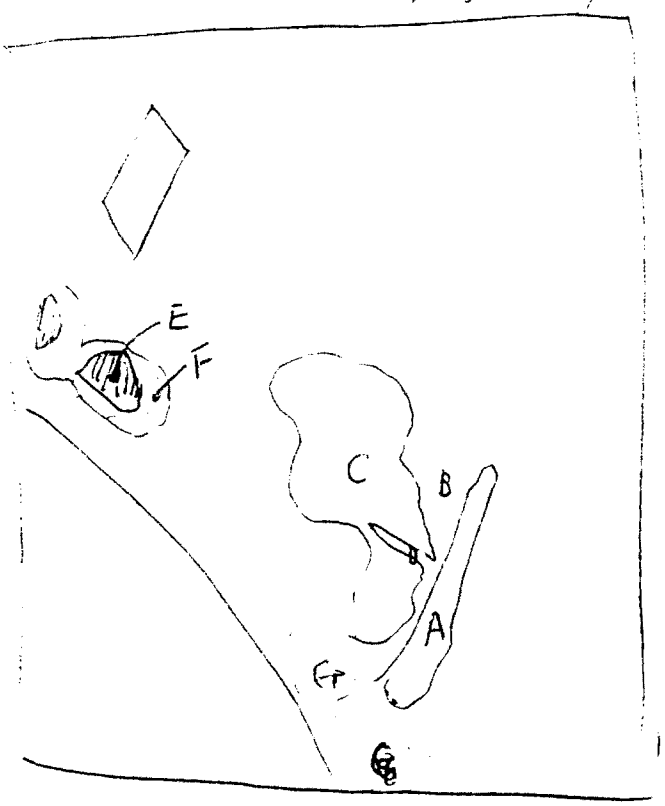
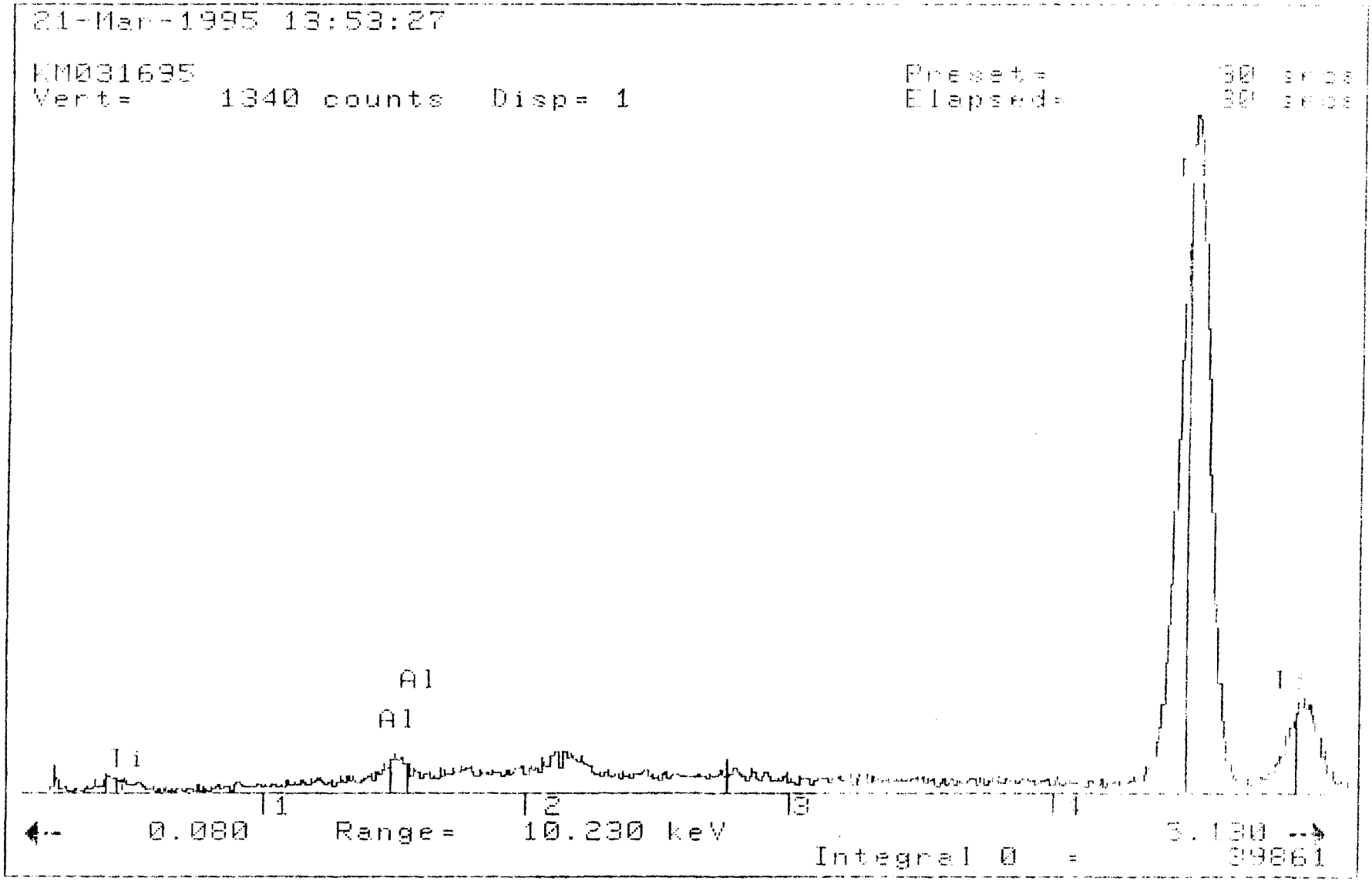
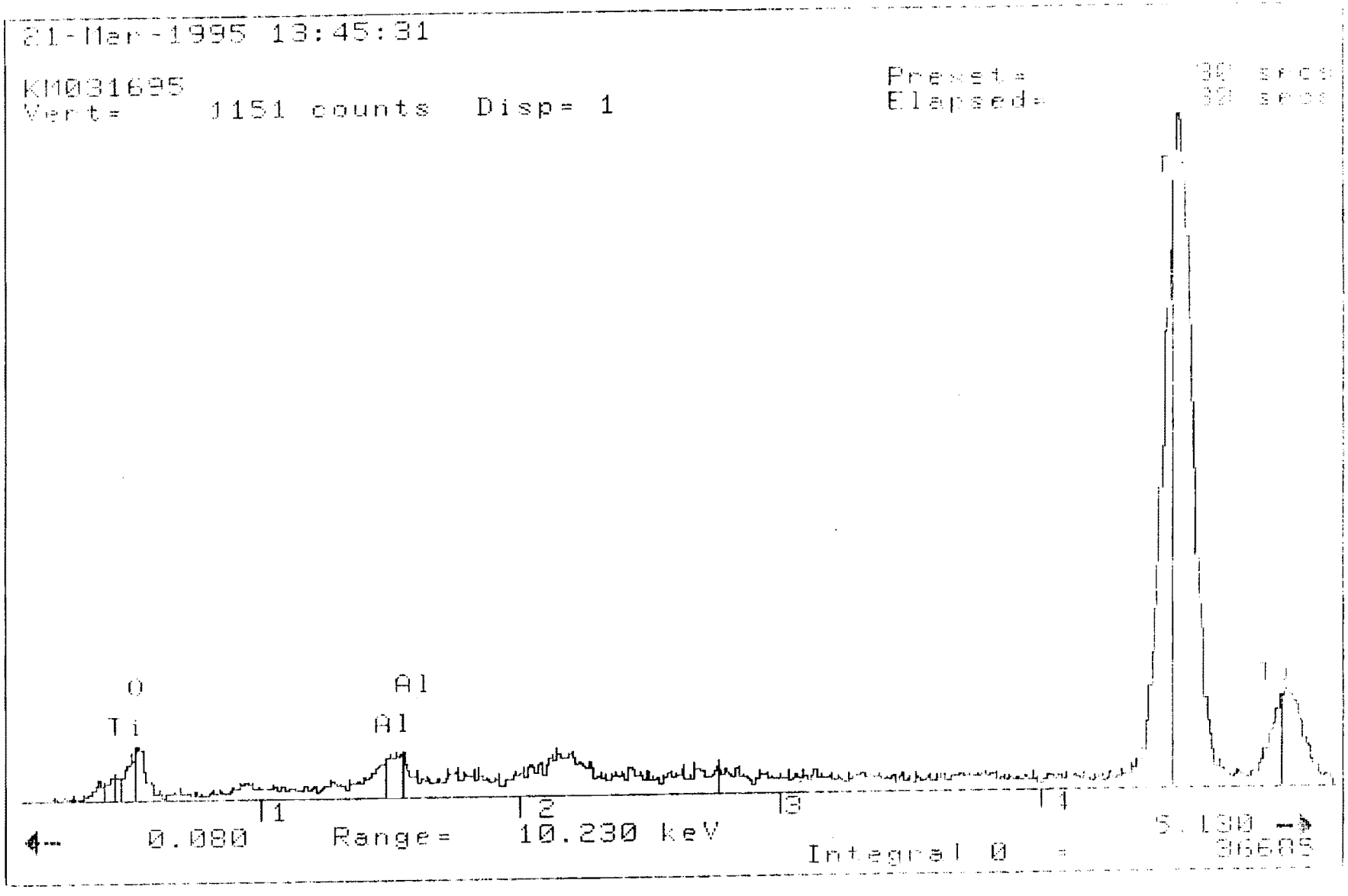


Figure 4

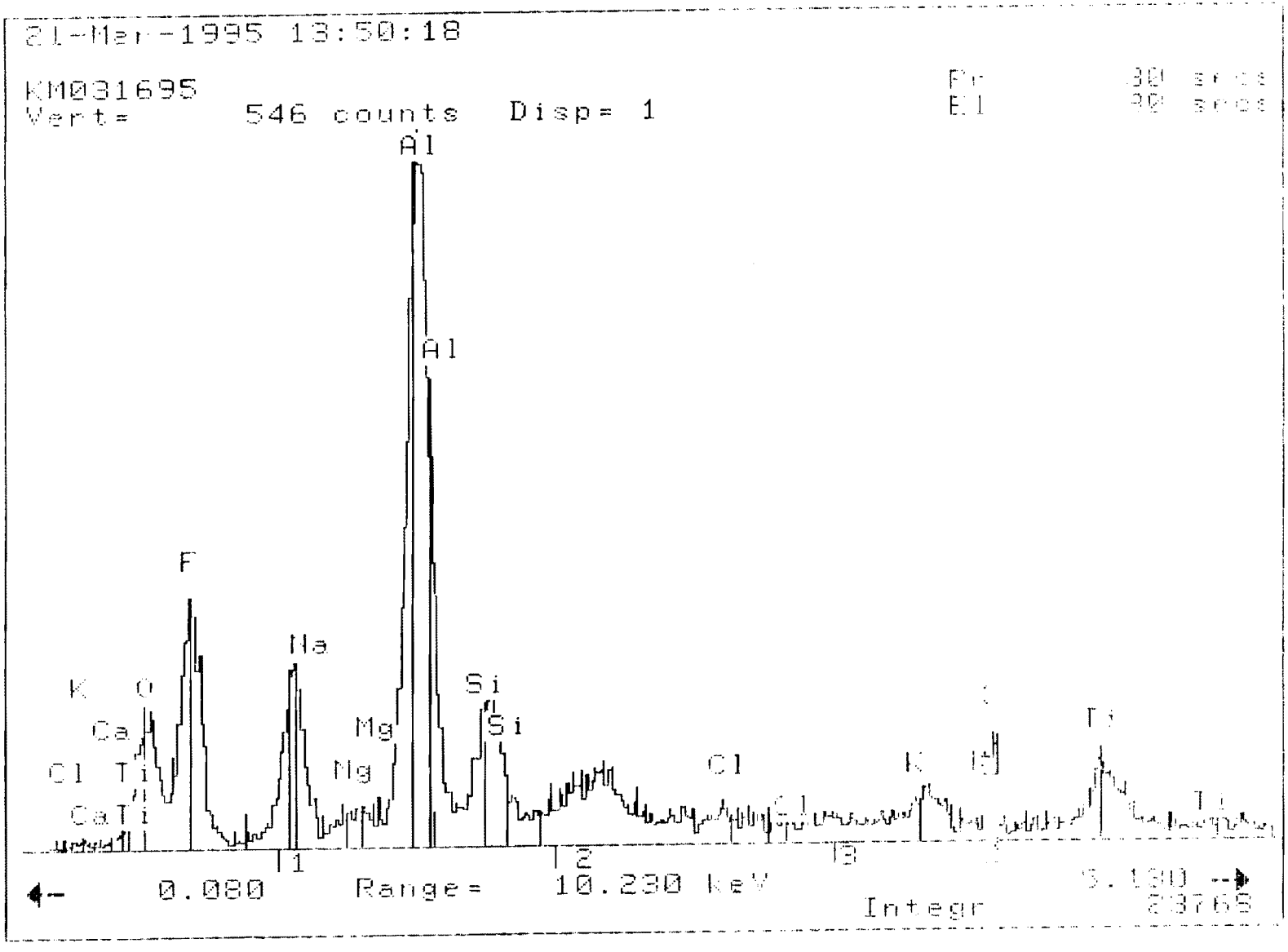


G: less dark than A

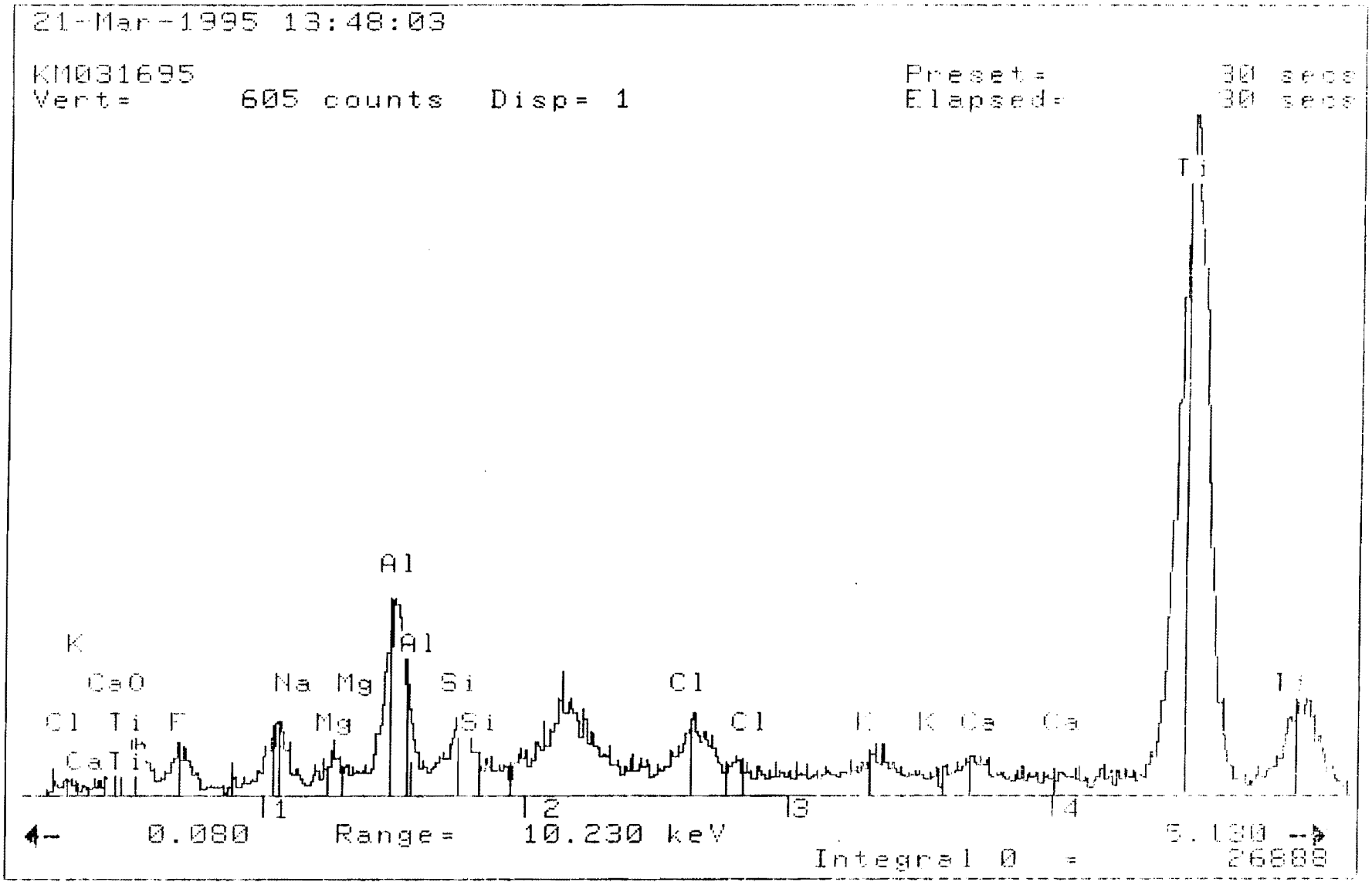

21-Mar-1995 13:53:27
KM031695
Vert= 1340 counts Disp= 1
Preset=
Elapsed=
Al
Al
1
2
3
0.080
Range= 10.230 keV
3.130
Integral 0 =
39861



~~Circular area~~
Facet area

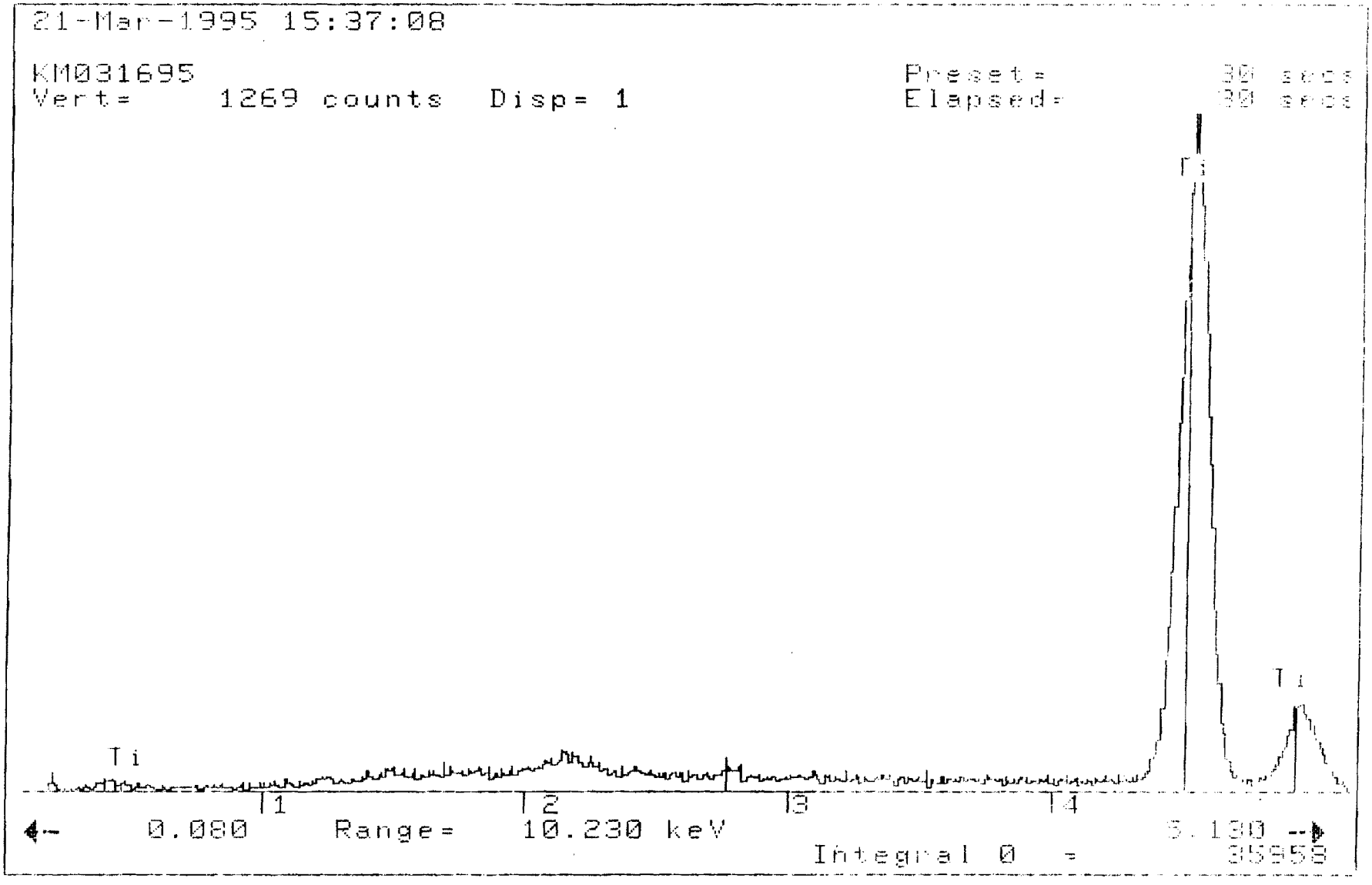

21-Mar-1995 13:50:18
KM031695
Vert= 546 counts Disp= 1
Pr 30 secs
El 30 secs
Al
Al
F
Na
K
O
Ca
Cl
Ti
Ca Ti
Mg
Mg
Si
Si
Cl
K
Ti
1
2
0.080
Range= 10.230 keV
5.130
Integr 83765

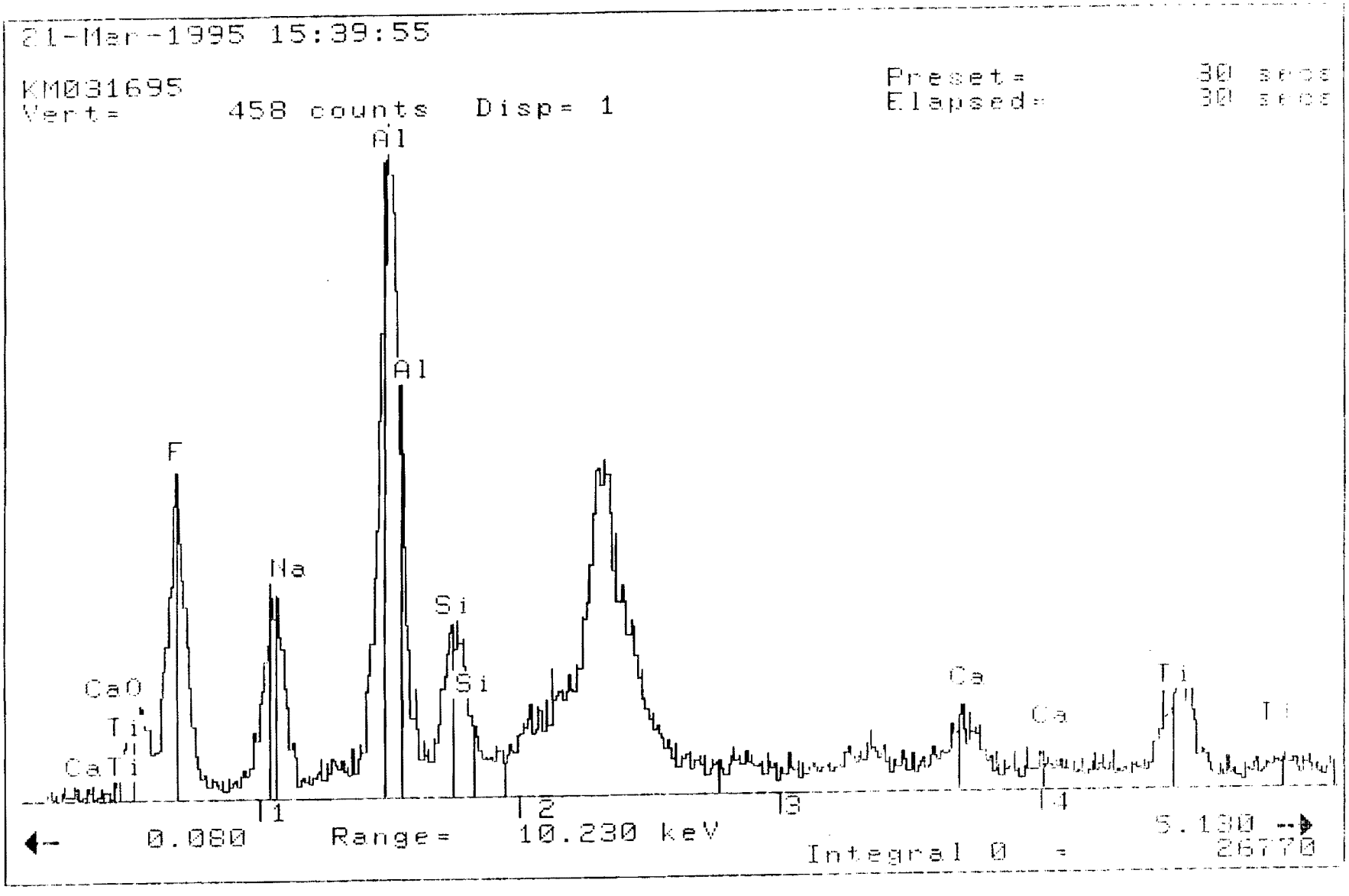
Sec



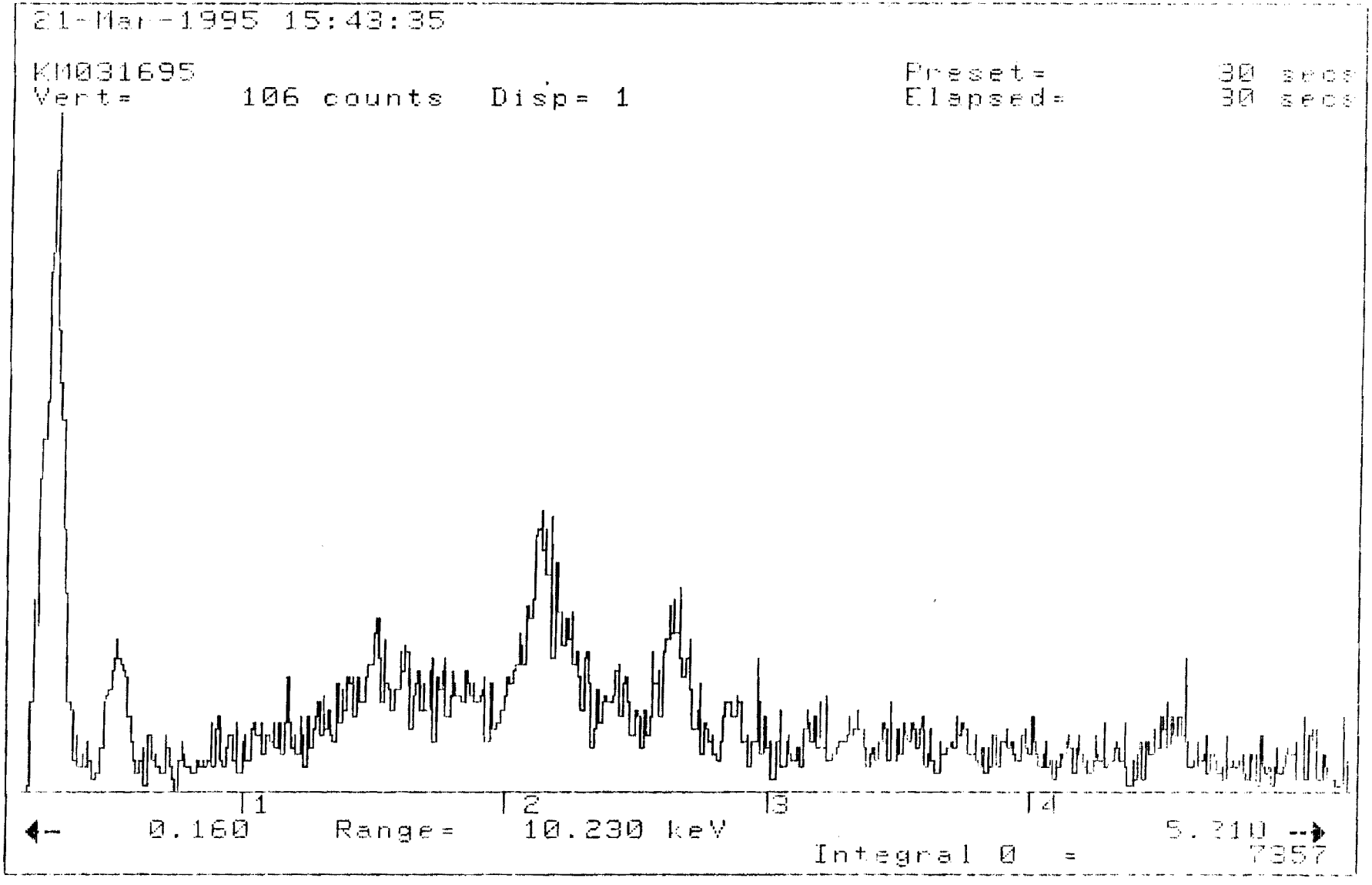
Circular area

A

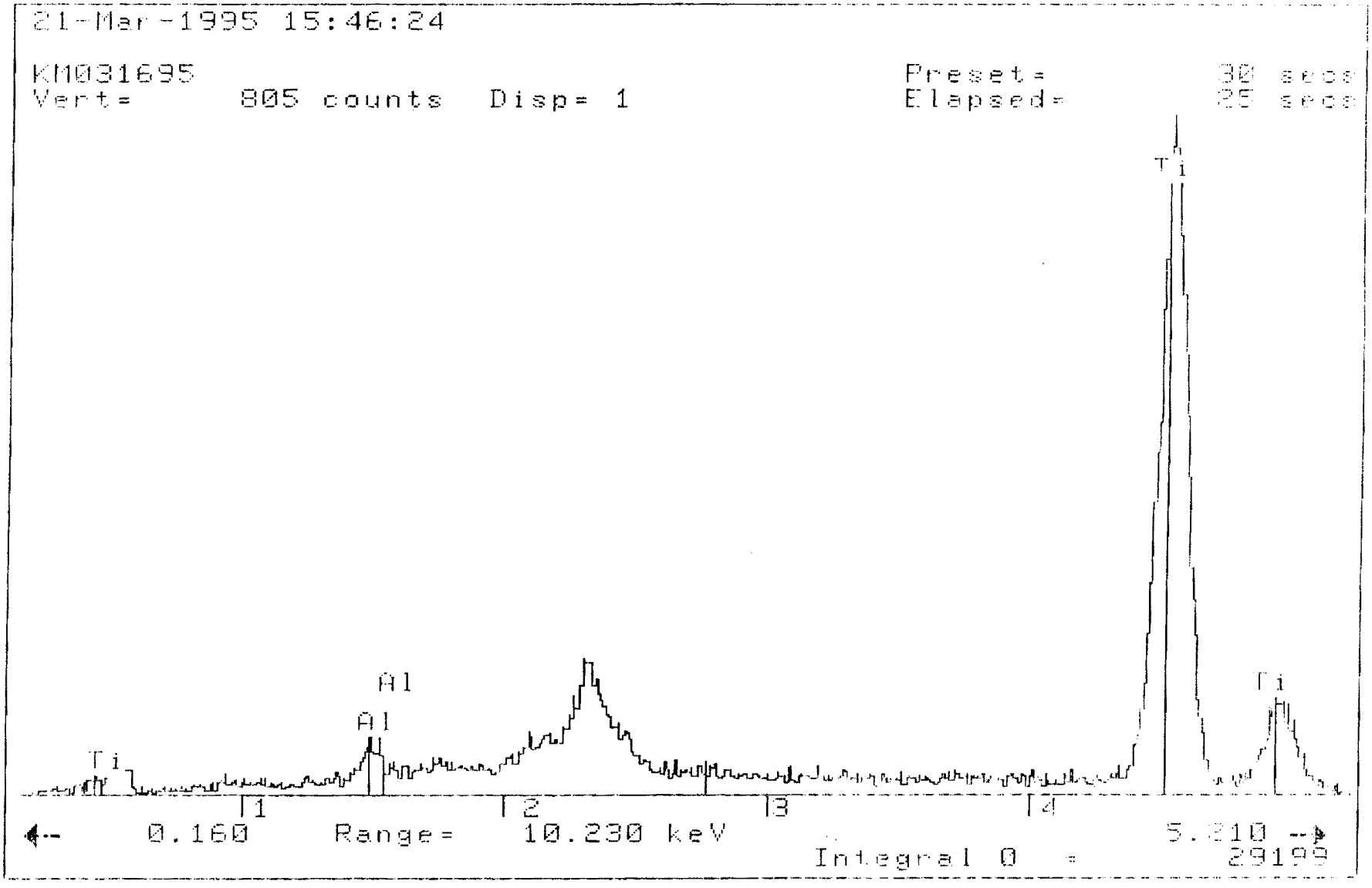

21-Mar-1995 15:37:08
KM031695
Vert= 1269 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
Ti
Ti
Ti
1
2
3
4
0.080 Range= 10.230 keV 5.130
Integral 0 = 35958


21-Mar-1995 15:39:55
KM031695
Vert= 458 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
Al
Al
F
Na
Si
Si
CaO
Ti
CaTi
Ca
Ca
Ti
Ti
1
2
3
4
0.080
Range= 10.230 keV
5.130
Integral 0 = 26770

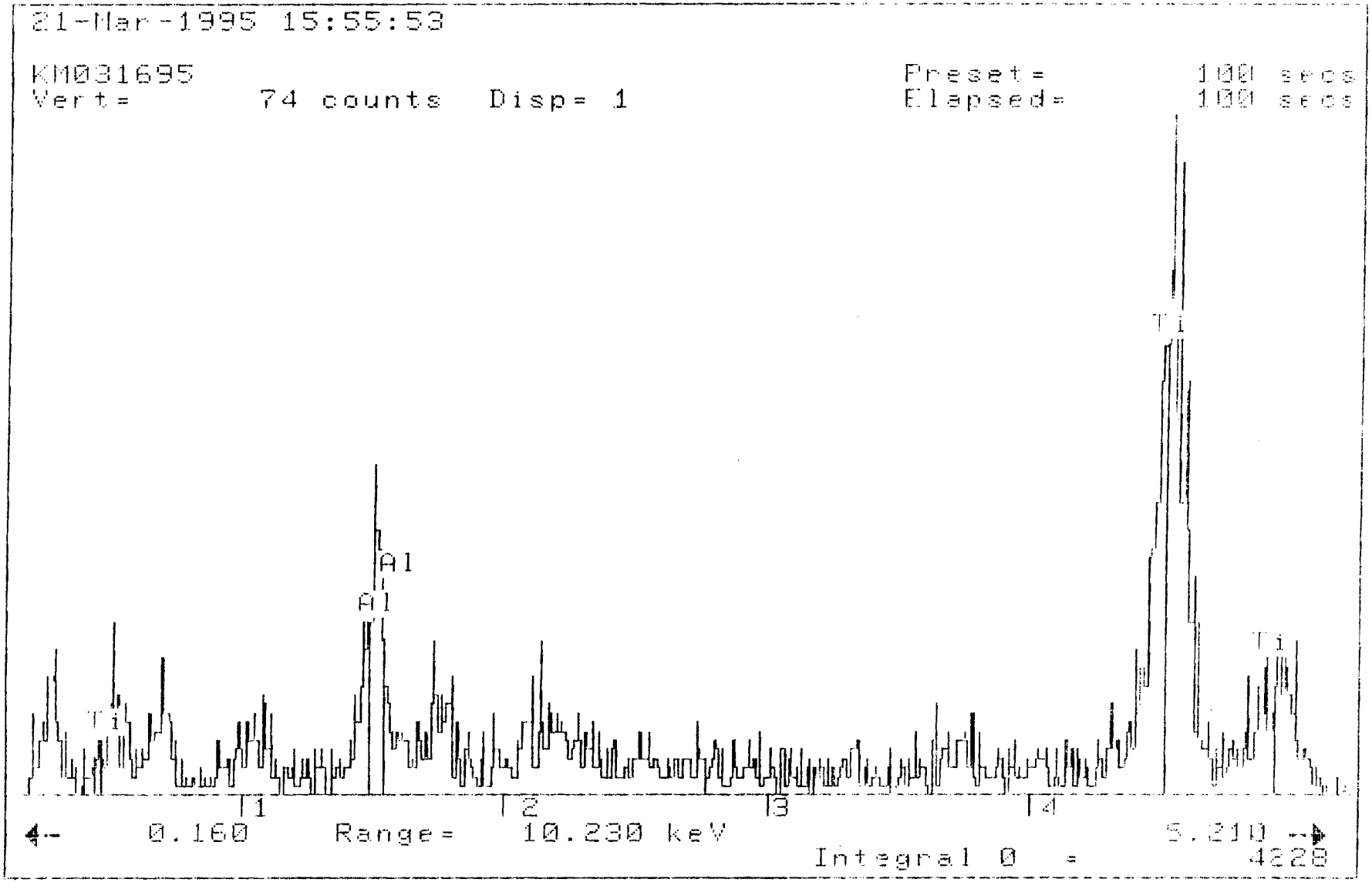
C

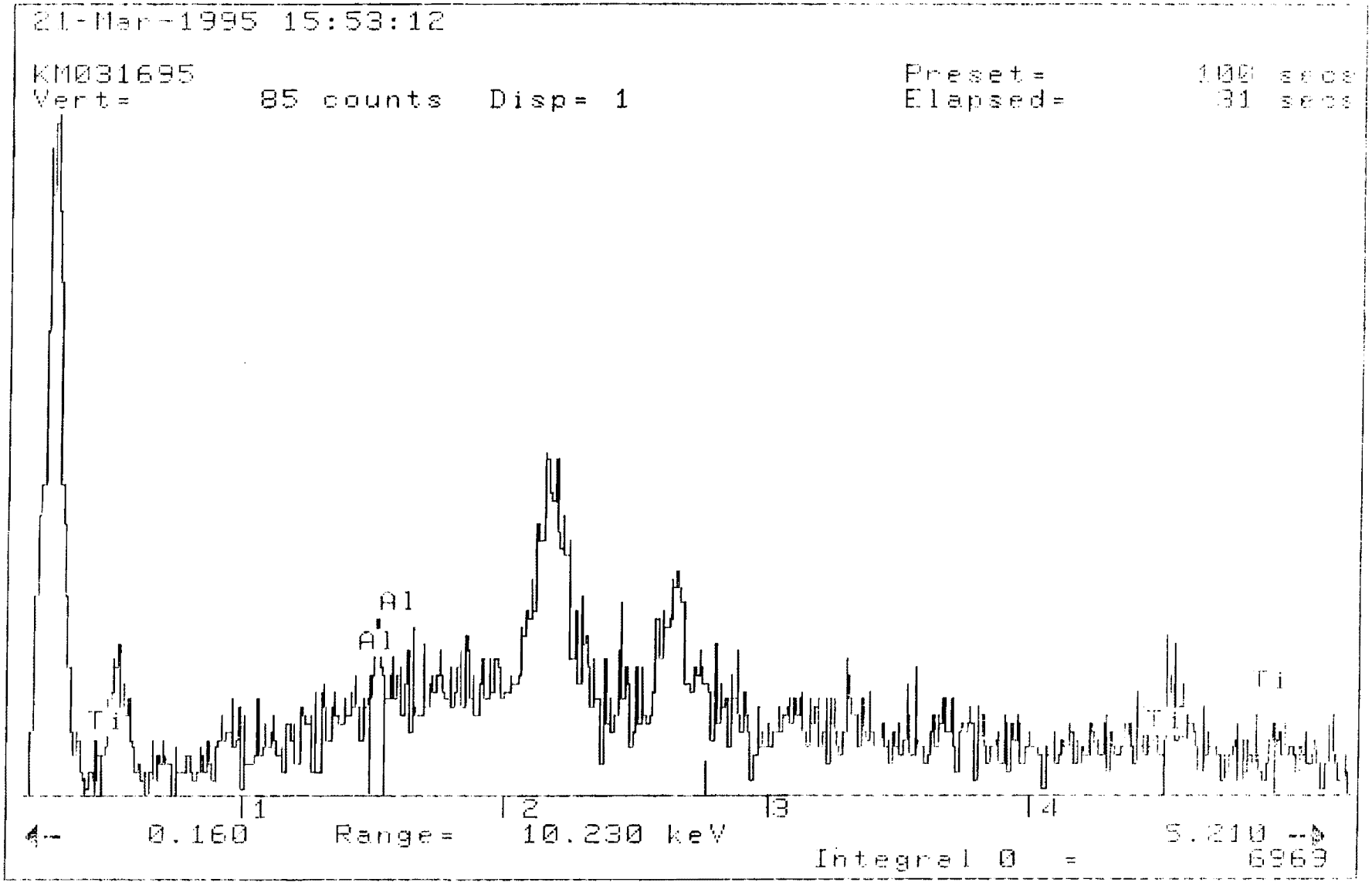

21-Mar-1995 15:43:35
KM031695
Vert= 106 counts Disp= 1
Preset= 30 secs
Elapsed= 30 secs
1
2
3
4
0.160 Range= 10.230 keV 5.210
Integral 0 = 7357

Epoxy


21-Mar-1995 15:46:24
KM031695
Vert= 805 counts Disp= 1
Preset= 30 secs
Elapsed= 25 secs
Ti
Ti
Al
Al
Ti
1
2
3
4
0.160
Range= 10.230 keV
Integral 0 = 29199

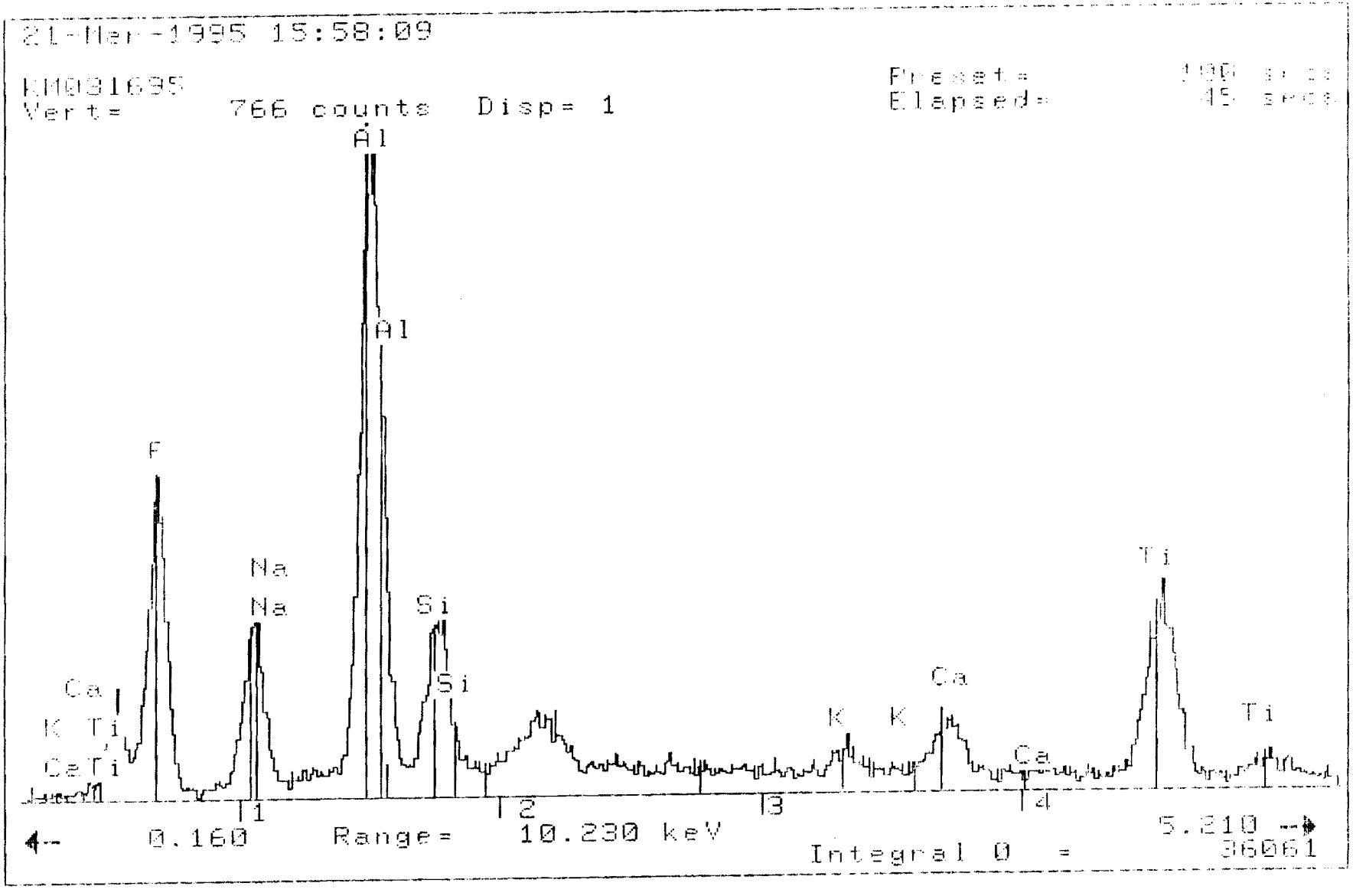
E


21-Mar-1995 15:55:53
KM031695
Vert= 74 counts Disp= 1
Preset= 100 secs
Elapsed= 100 secs
Ti
Al
Al
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 = 4228


21-Mar-1995 15:53:12
KM031695
Vert= 85 counts Disp= 1
Preset= 100 secs
Elapsed= 31 secs
Al
Al
Ti
Ti
Ti
1
2
3
4
0.160 Range= 10.230 keV 5.210
Integral 0 = 6963

Epoxy

G


21-Mar-1995 15:58:09
KM031695
Vert= 766 counts Disp= 1
Preset=
Elapsed=
Al
Al
F
Na
Na
Si
Si
Ca
K Ti
Ca Ti
K K
Ca
Ca
Ti
Ti
1
2
3
4
0.160
Range= 10.230 keV
5.210
Integral 0 =
36061

	MTO Ir	Ir/Slope (Wt%)	MBO Ir	Wt%	MgO Ir	Wt%	TiB2 Ir
Mg1(-325)	0.0853	3.888112	0.2234	20.82923	2.8681	65.61796	1.1476
Mg2(-100)	0.1452	6.618451	0.1661	15.48673	2.4129	55.20365	0.9839
Mg3(-50)	0.1217	5.547283	0.1984	18.4983	1.9656	44.97007	0.7407
Mg4(-6)	0.1302	5.934727	0.1367	12.74555	1.2316	28.17722	0.5563
Mg5(-6)	0.1318	6.007658	0.1907	17.78037	0.9225	21.10546	0.4791
Mg6(-50)	0.199	9.070743	0.1682	15.68253	1.8434	42.17432	0.8087
Mg7(-100)	0.0808	3.682995	0.0769	7.169954	1.1308	25.87106	0.4423
Mg8(-325)	0.19	8.660508	0.1697	15.82238	1.979	45.27665	0.8322

0.1541
0.1664
0.1281
0.129
0.1579
0.2
0.1557
0.2388
0.1589
0.1613
0.1735

Original (to be returned to Shin)

Characterization of TiB_2 Electrode # 4 (As-Pressed)

Hyunho Shin

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March 29, 1995

I Introduction

The electrode # 3 showed a sodium and oxygen-rich stone like area formed by the diffusion of cryolite melt content. Therefore, it was necessary to characterize the as-pressed TiB_2 electrode material as a comparison standard. The as-pressed electrode was densified at 1580°C and then fabricated using the EDM.

II Experimental Procedure

The as-received electrode (from Joel through Kathryn and Gautam) was cut using Speyer's high speed saw with diamond blade (2hrs). The cut piece was mounted using epoxy and hardener (overnight) followed by rough polishing using diamond wheel/SiC paper and fine polishing using diamond past (2 hrs). The polished specimen surface was cleaned using an ultrasonic cleaner (20 min) and then coated with gold in a vacuum sputtering chamber (1hr). The coated sample surface was characterized using SEM/EDS/BEM(Backscattered Electron Microscopy) and Image Mapping (4 hrs).

III Results

As shown in Figure 1, the sample was very porous. In addition to the porous rough surface area, an apparent pore channel (4~5 μm in diameter) is observed in the figure. Figure 2 shows another pore with its detailed microstructure. This pore shows very fine (submicronsize) particles. These particles are similar to the as-leached TiB_2 powder. Since the pore surface itself was not receiving the pressure during hot pressing (bridging effect by other growing crystals of whisker shape), these particles did not get a chance of pressure induced grain growth. However the pores shown in Figures 1 and 3 is believed to be formed by bridging crystals.

Figure 3 shows backscattered electron micrograph of the sample. Three distinct areas are apparent — bright area, gray area, and grain boundary phase. As shown in the attached EDS results, the gray areas were, in general, rich in titanium with appreciable oxygen. The bright areas showed titanium element only. The grain boundary phase did not give any difference from the gray area. This was because the EDS electron beam was interacting with bigger volume of the sample than the volume of the grain boundary phase. The elemental image map did not form any appreciable shape on the screen. This is the case when no apparent chemical contrast is present in the investigating area.

The brightness difference in the backscattered mode is resulted largely from the presence of appreciable (but not enough to form an image map) oxygen element. It is interpreted that the matrix area is first achieved by the pressure induced densification of fine TiB_2 particles bearing an appreciable oxygen. Then the bright oxygen free TiB_2 grain is interpreted to grow from oxygen-bearing TiB_2 matrix area during hot pressing. Figure 4 indicates that the

gray area is the matrix area.

IV Recommendation

It is recommended to characterize the as-leached powder surface in order to check the presence of appreciable oxygen element in the initial powder. It is also necessary to performe precise measurement of TiB_2 lattice parameters using XRD technique in order to confirm the contaimination.

Figure 1

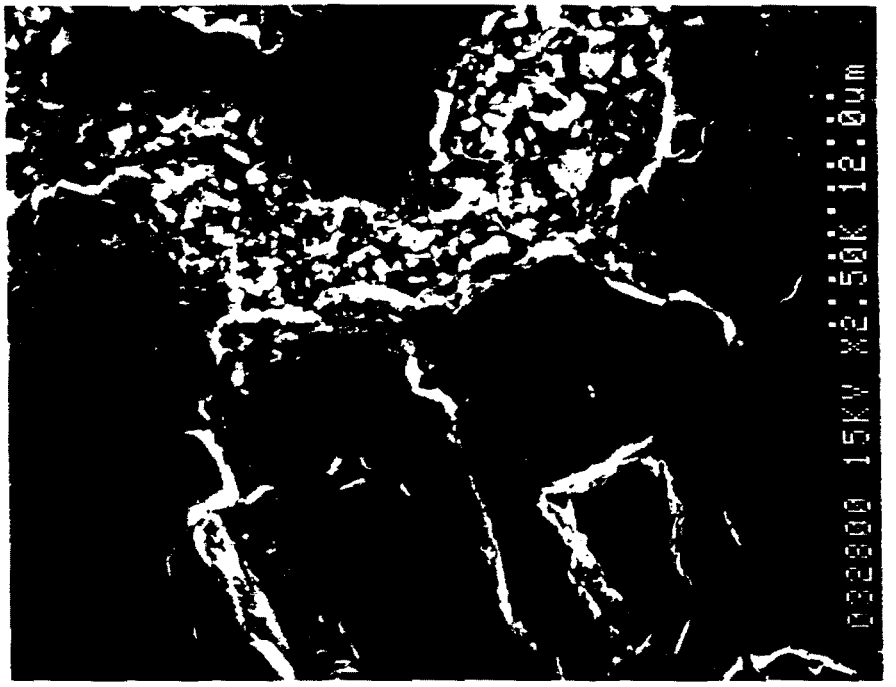


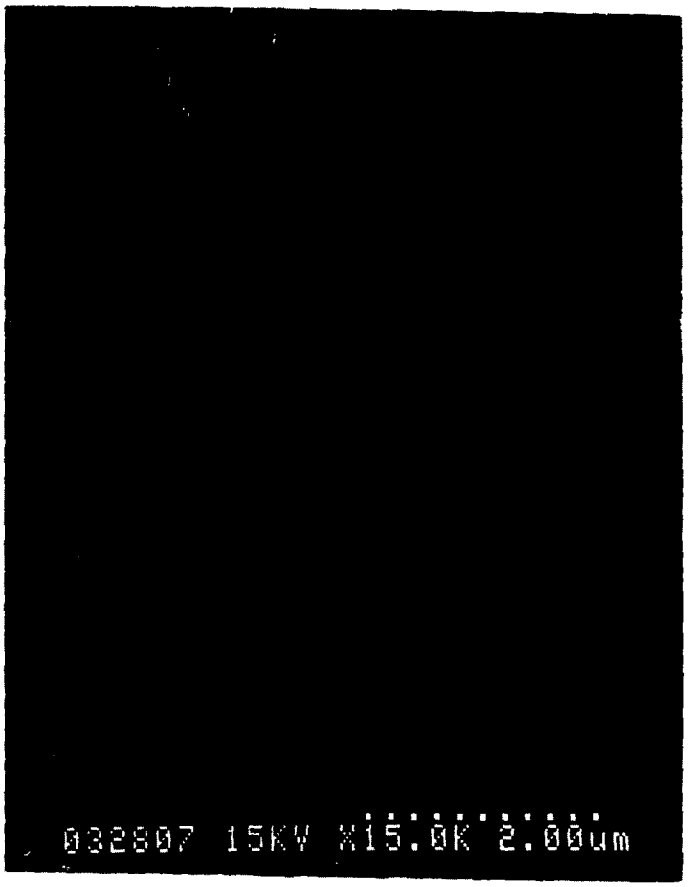
Figure 2

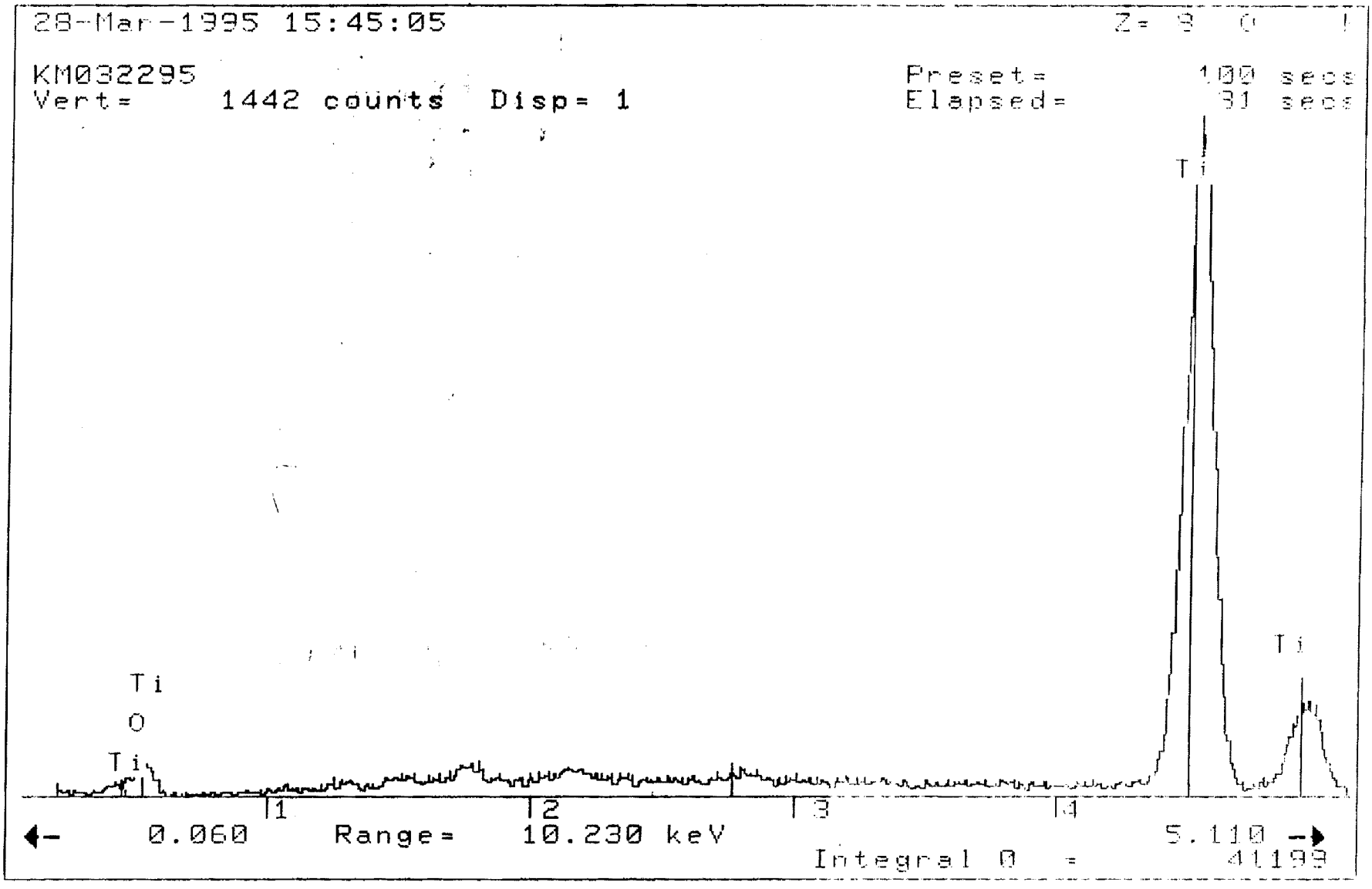
Figure 3

(a)

(b)

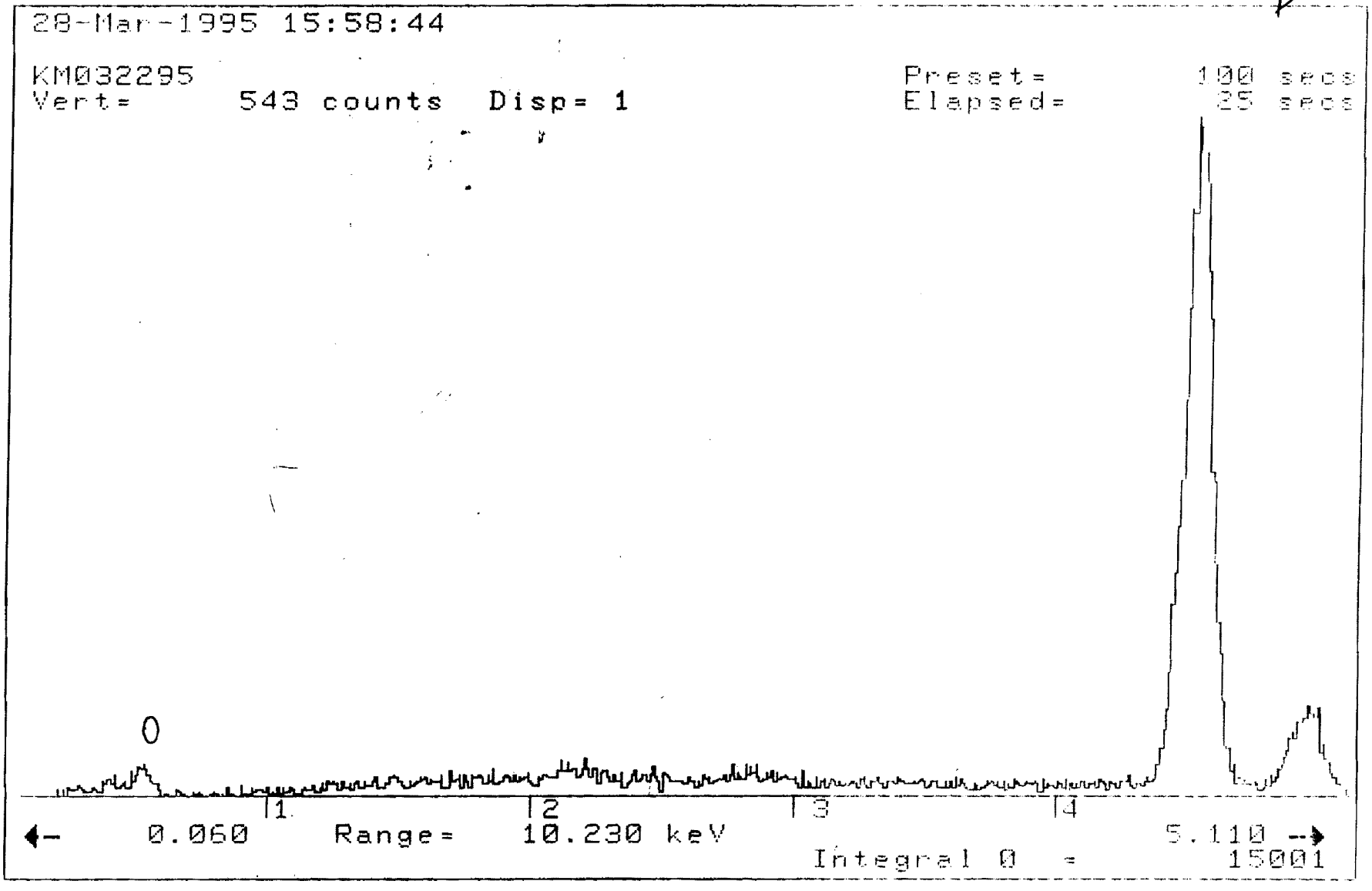
Figure 4



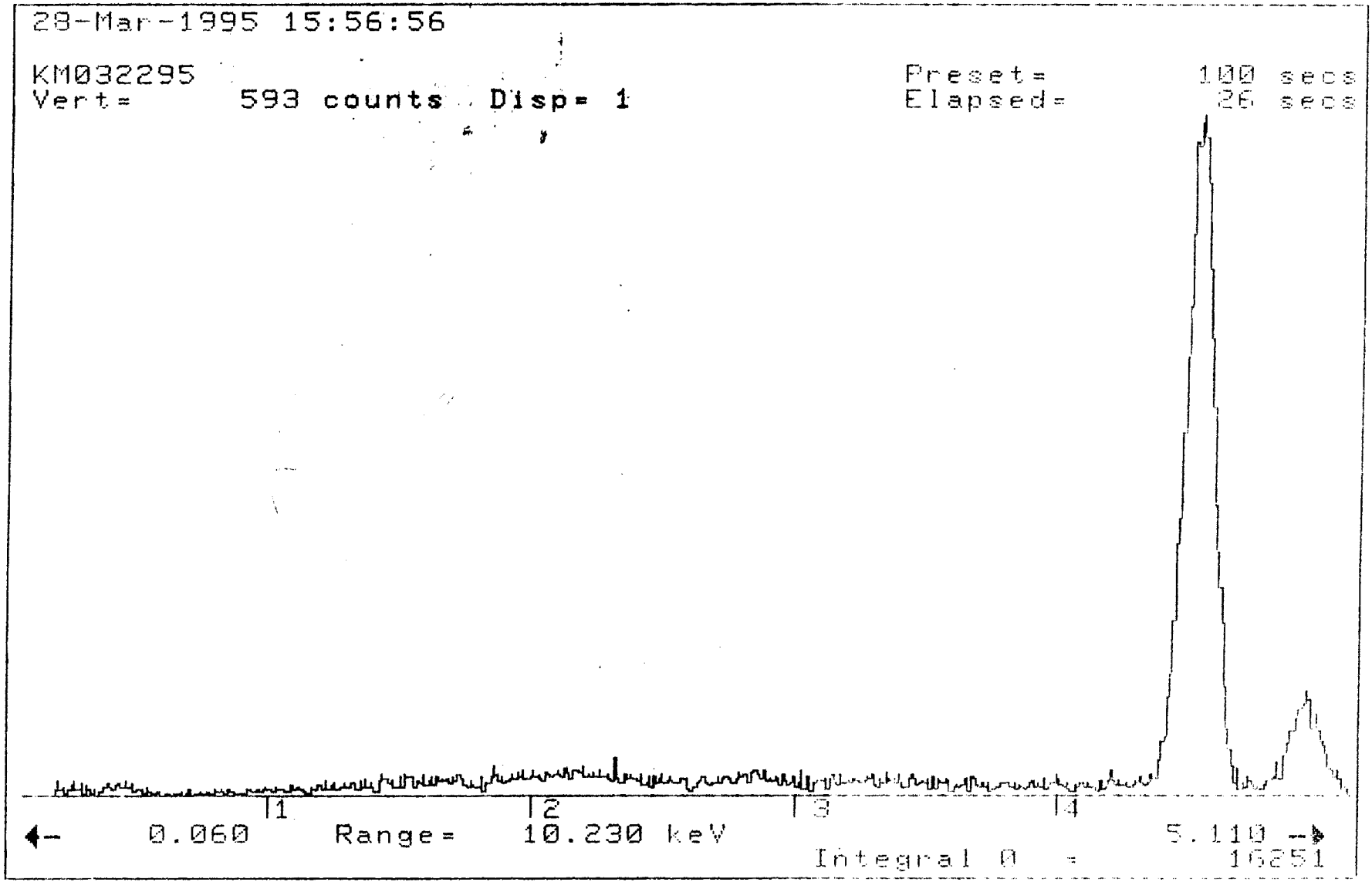


From Gray Area

Dark

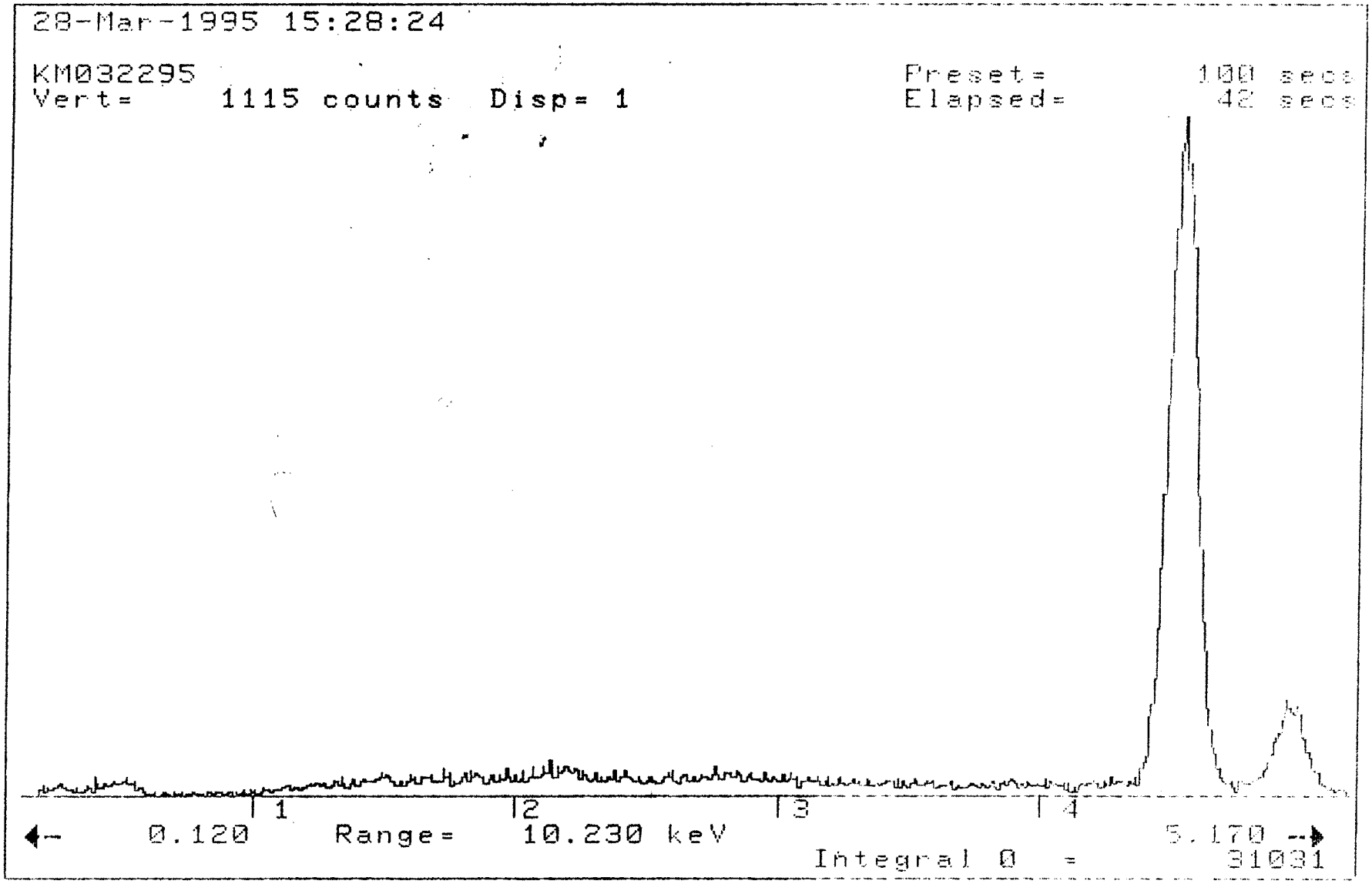


From Gray Area

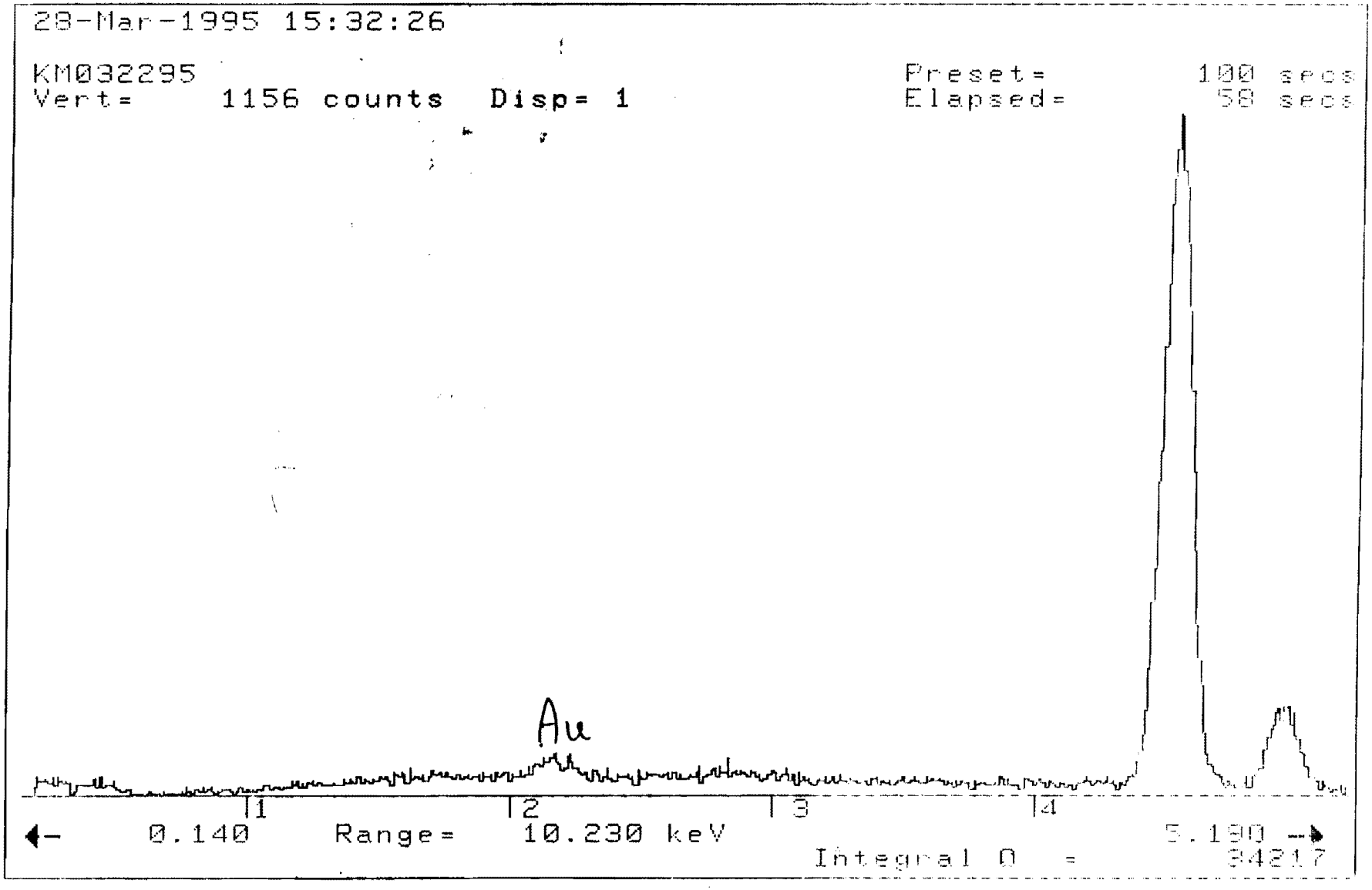


From Bright Area

(2)

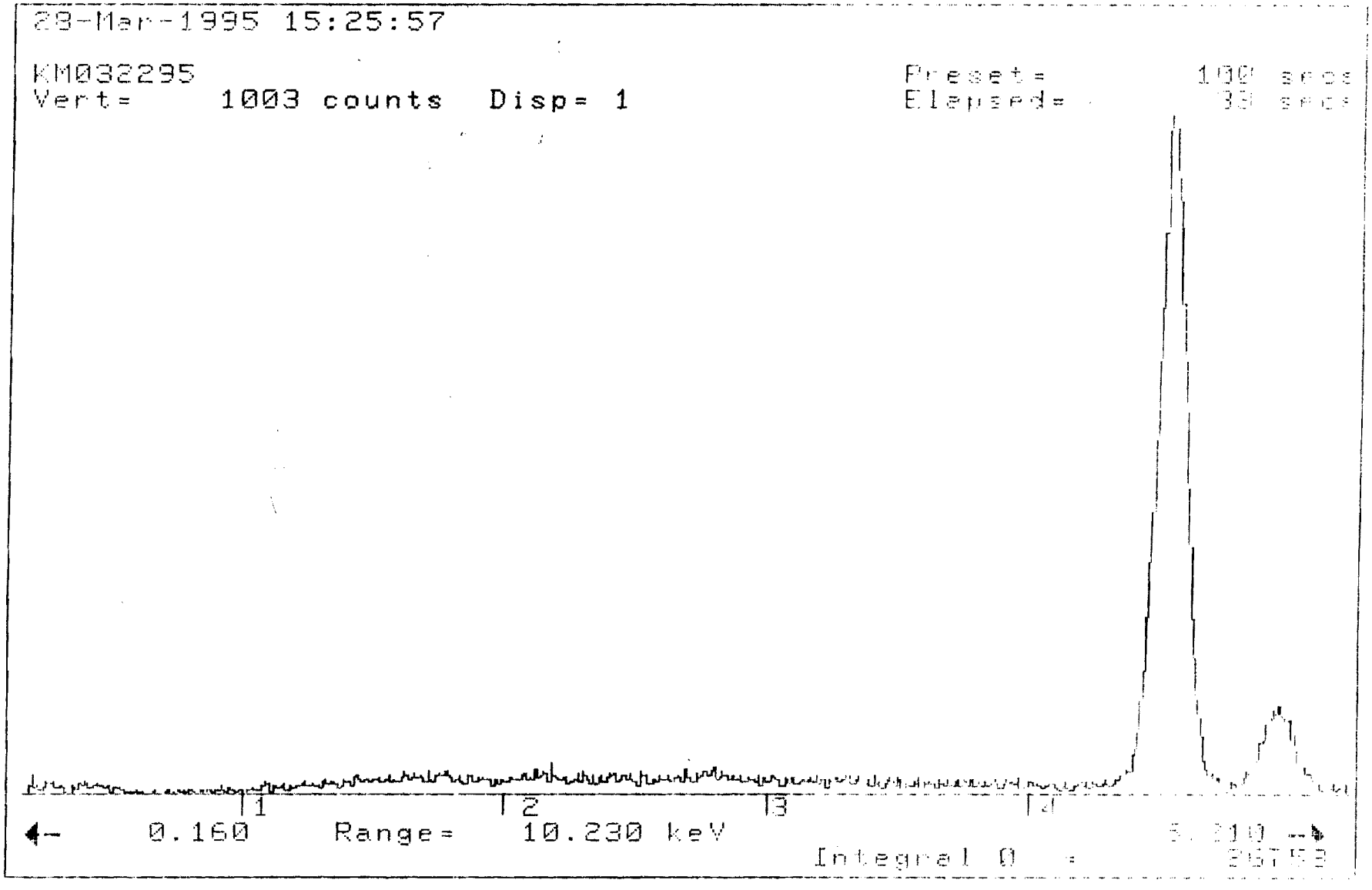


From Bright Area



From Grain Boundary phase

(1)



From Grain Boundary phase

File:xrdmgq.aem

Effect of Magnesium Particle Size Distribution on the Reaction Products in Mg-TiO_2-B_2O_3 Reaction System

April 3, 95

Hyunho Shin

School of Materials Science and Engineering,

Georgia Institute of Technology, Atlanta, GA 30332.

I Introduction

The reduction of TiO_2 and B_2O_3 to form TiB_2 depends on the reduction ability of magnesium particles such as particle size distribution, surface state, and purity, *etc.* The change of particle size is one of the most ambient way to tailor the reaction products via engineering the violent exothermic reaction. In the present work, the quantitative XRD results for reaction products with four different sizes of magnesium powder are presented.

II Experimental Procedure

100 g batch with 5 excess wt% B_2O_3 was thoroughfully mixed and shifted into slip cast silica crucible. The same length of nichrome wire was used for the ignition of each batch. This ensured to measure the required voltage to ignite each reactant powder batch. The first runs were done by Shin and Joel while the second runs were by Joel and William.

XRD calibration curves for TiB_2, MgO, Mg_2TiO_4, and $Mg_3B_2O_6$ were obtained after

Sample	TiB_2	MgO	$Mg_3B_2O_6$	Mg_2TiO_4
-325 mesh	18.8/13.6	65.6/45.3	20.8/15.8	3.9/8.7
-100 mesh	16.1/	55.2/	15.5/	6.6/
-50 mesh	12.1/13.2	45.0/42.2	18.5/15.7	5.5/9.1
-6 mesh	9.1/7.8	28.2/21.1	12.7/17.8	5.9/6.0

Table 1: XRD quantitative analysis results of the reaction products with different particle size Mg. First Run/Second Run. Numbers represent their weight percent. The samples from the second runs were not ensured to be the representative of the whole reaction product while the samples from the first runs were ensured.

considerable efforts. The maximum peak height of the primary peak height of each phase was used for the construction of the calibration curves. The absolute value of the quantitative analysis results depends upon the purity of the standard sample while the relative trend of percentage of each phase among different reaction products is correct.

III Results

As the particle size of the Mg powder increased, a higher variac voltage was required. Table 1 shows the quantitative XRD results of the reaction products with different particle size Mg.

Joel said the second run of the -100 mesh sample contained more than 20 wt% CaF_2 standard. This resulted in a smaller weight percentage of the products in the second run of the -100 mesh sample. The samples for the second runs were not from the homogenized product batch while the XRD samples of the first runs were ensured to be the representative of each reaction product.

Quantitative Ananlysis of Samples Obtained by Various Leaching Process

— Hyunho Shin —

April 17, 1995

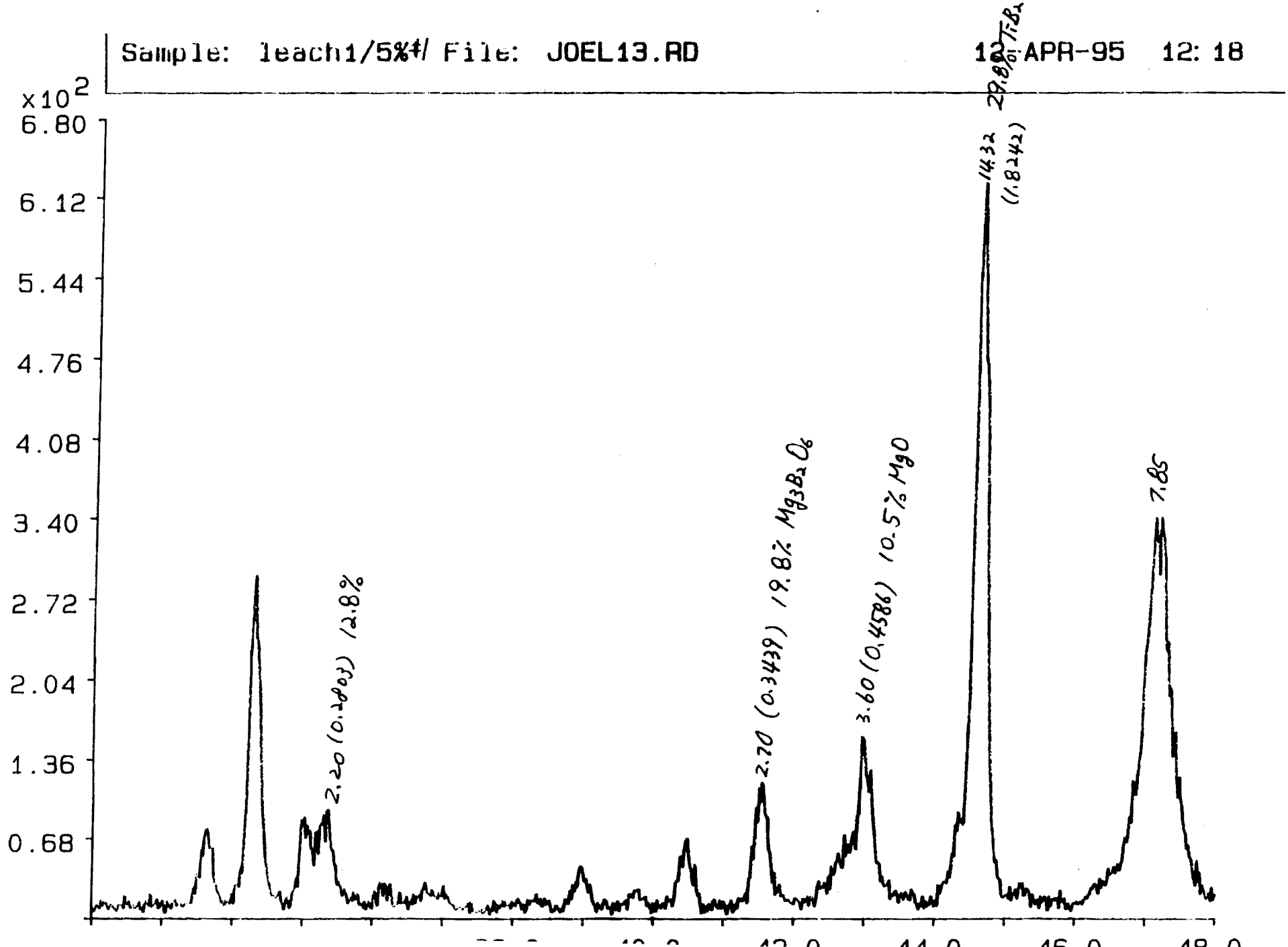
Ginorsborate

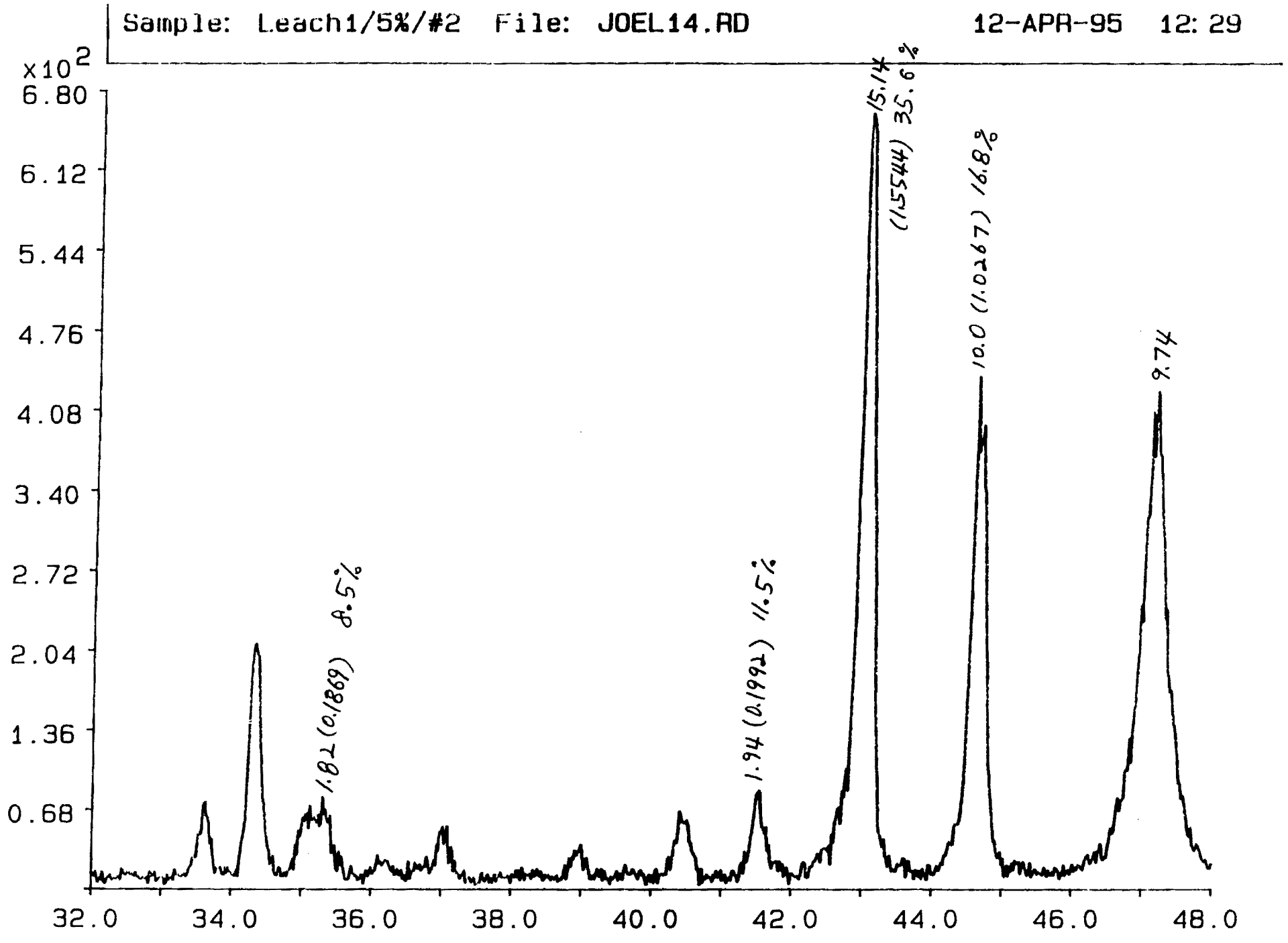
	Ratio	TiB_2	Ratio	MgO	Ratio	$Mg_3B_2O_6$	Ratio	$MgTiO_4$	Amorphous
#1	1.8242	29.84002	0.4586	10.4921	0.3439	19.80215	0.2803	12.77653	27.0892
#2	1.0267	16.79462	1.5544	35.56242	0.1992	11.47016	0.1869	8.519205	27.6536
#3	2.193	35.8728	1.402	32.07572	0.3056	17.59679	0.0906	4.129695	10.32499
#4	1.7642	28.85855	0.351	8.030371	0.3342	19.24361	0.3484	15.88064	27.98683
#5	3.15625	51.62952	0.1771	4.051791	0.2292	13.1976	0.25	11.39541	19.72569
#6	0.7669	12.54485	1.8698	42.77831	0.1602	9.224497	0.1666	7.593898	27.85845
#7	0.9624	15.74281	3.0292	69.3037	0.1608	9.259046	0.0772	3.518901	2.175543
#8	5.1943	84.96767		0	0.26	14.97109		0	0.06124
#9	3.4174	55.90137	0.8532	19.51998	0.2867	16.50851		0	8.070139
#10	4.1192	67.38132		0		0		0	32.61868
#11	1.0182	16.65558	2.5418	58.15269	0.2069	11.91354	0.2	9.116324	4.161865
#12	4.5806	74.92884	0.2258	5.165976	0.2258	13.00182		0	6.903361
#13	4.003	65.48054	0.1829	4.184487	0.2743	15.7945		0	14.54047

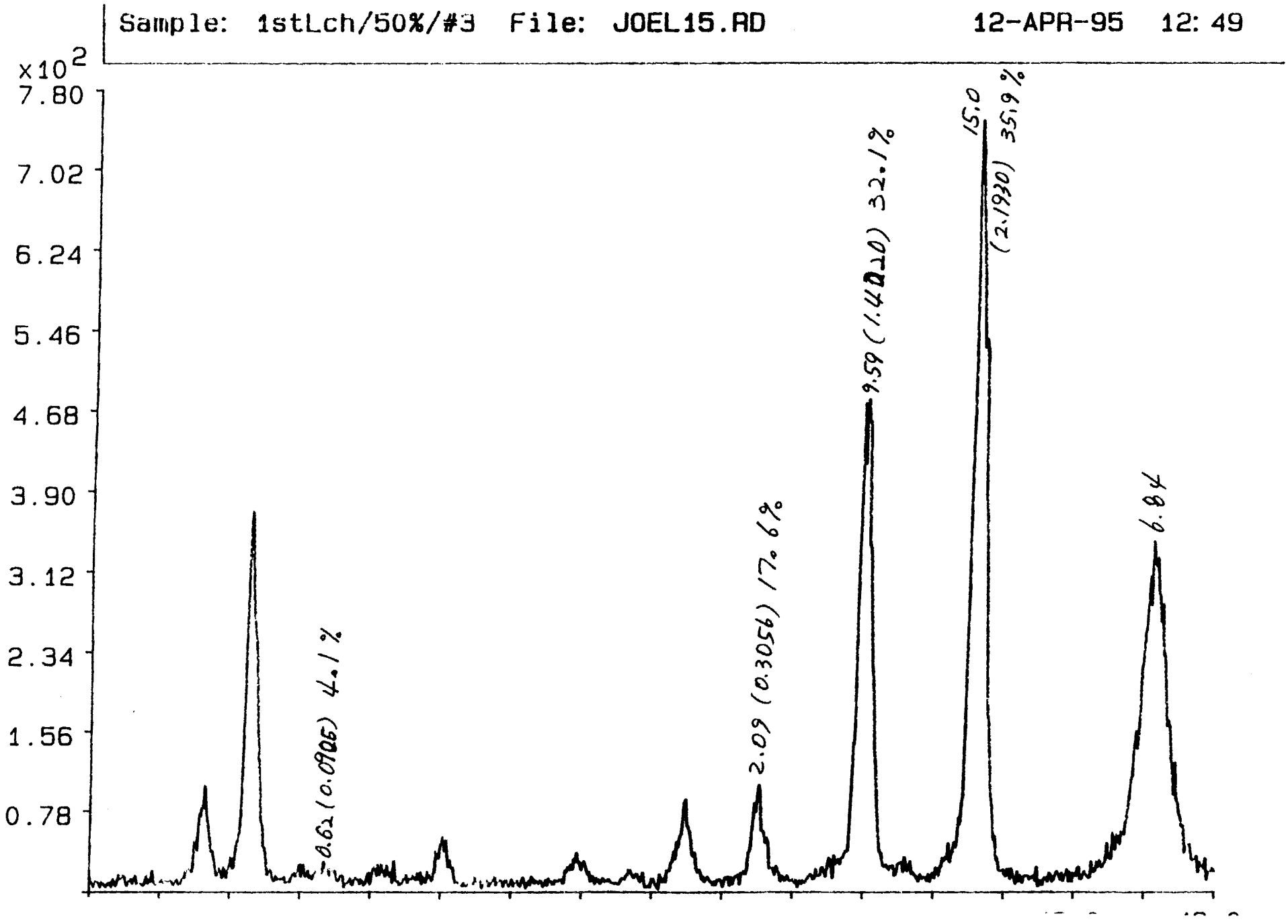
increase

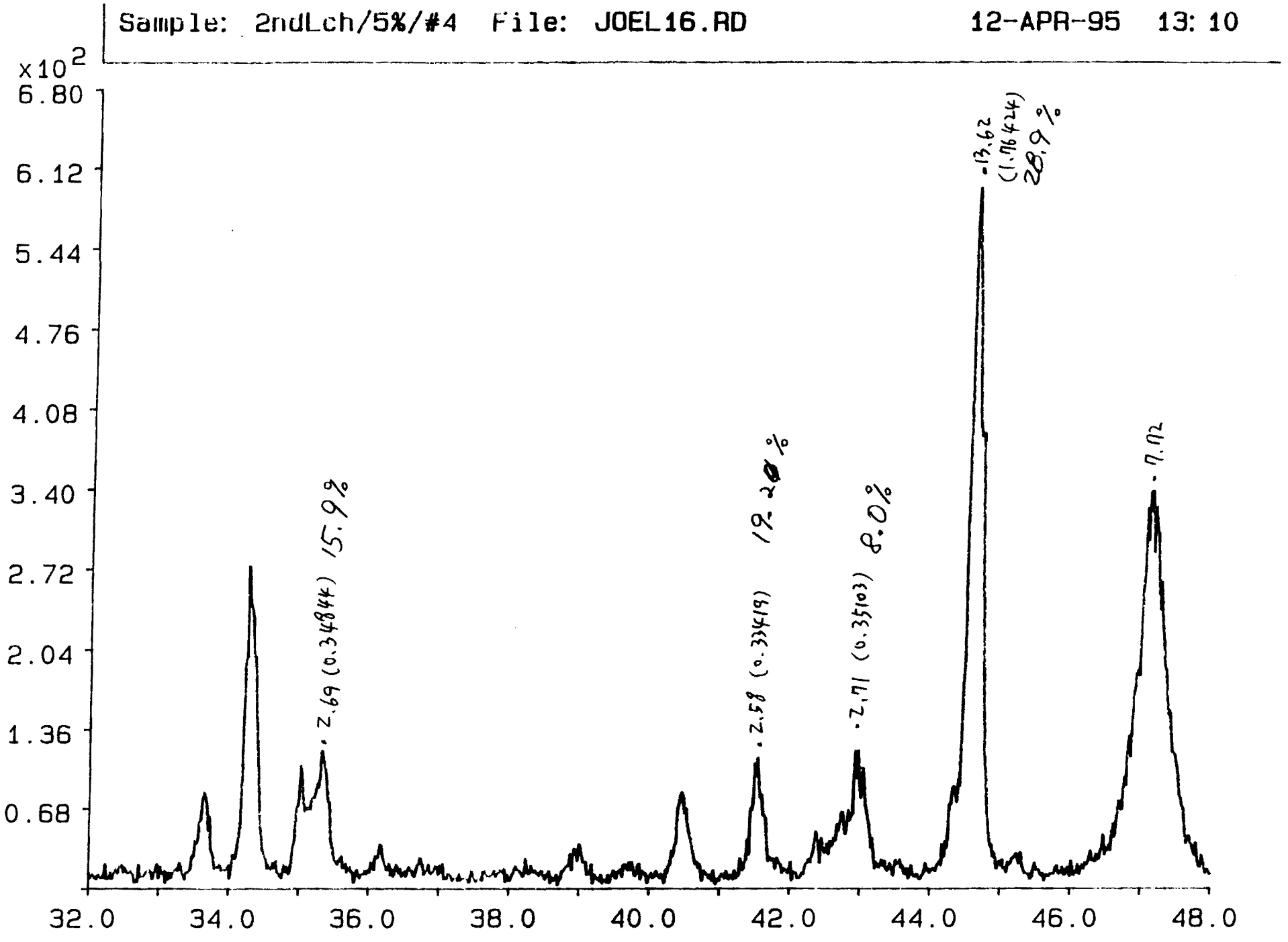
#1 : 30 g powder per liter, leached at 50°C, pH of 2.

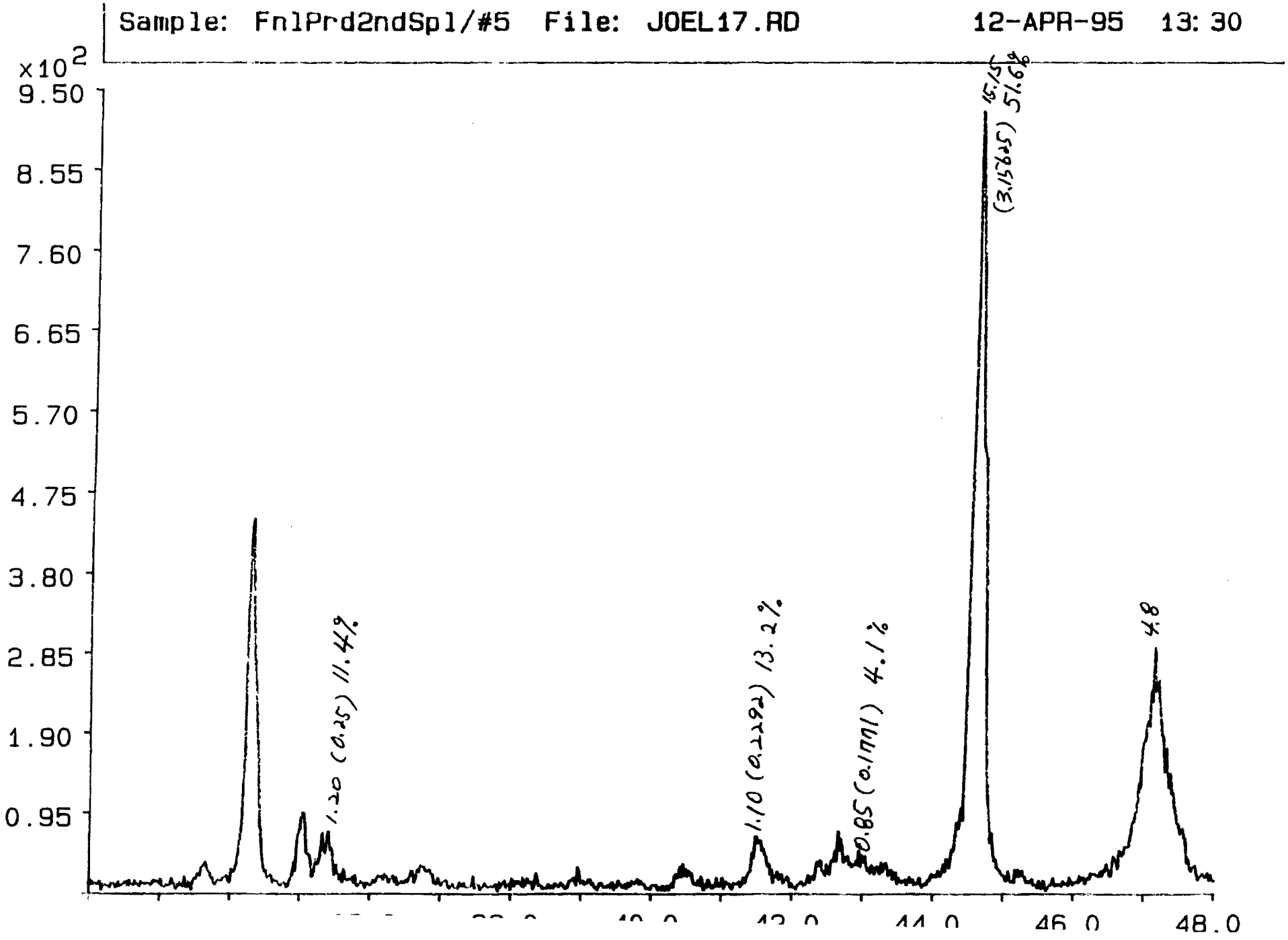
#12 : Very high powd. Concentration, leached at 90°C, pH of 2.

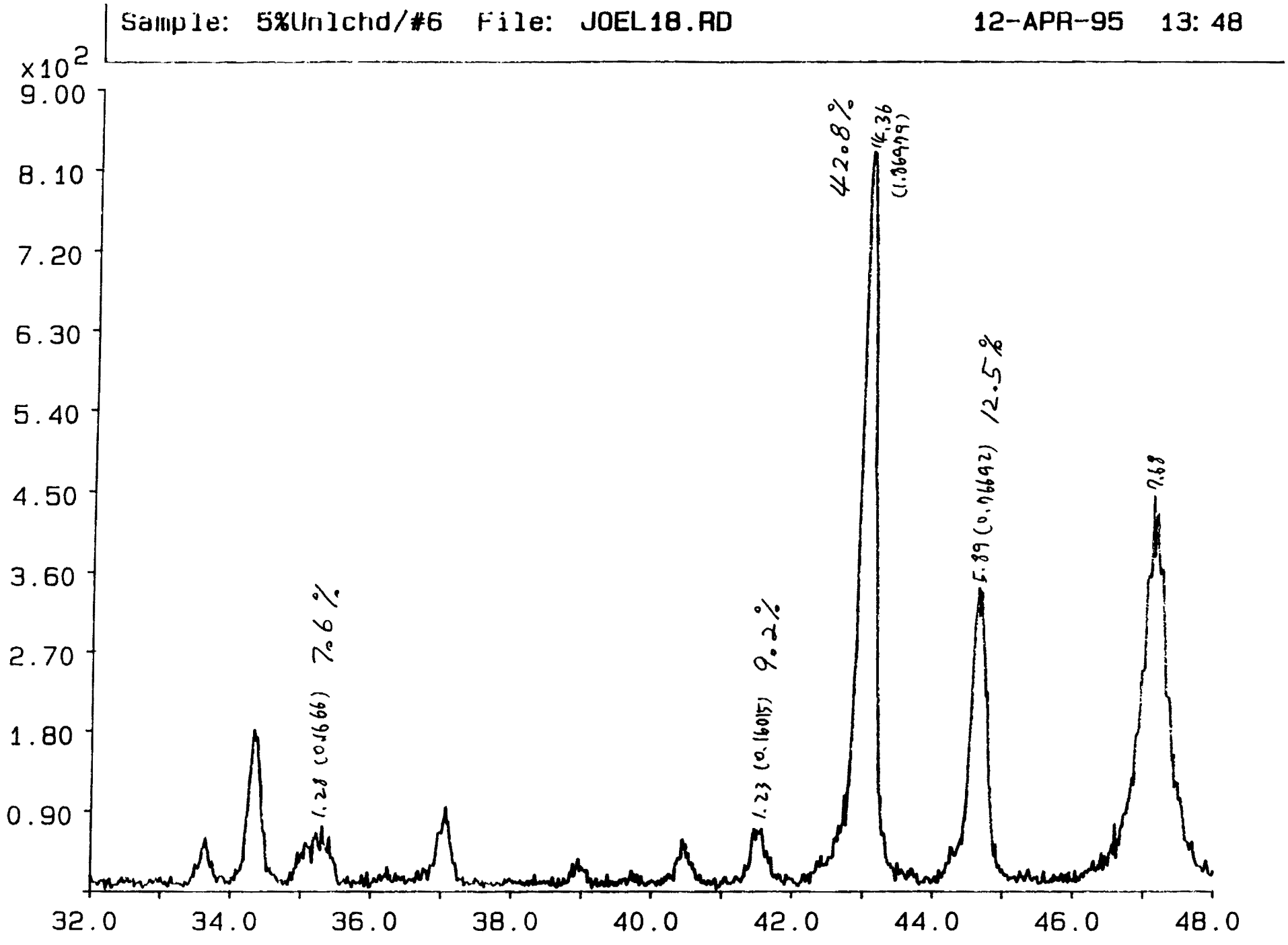

Sample: leach1/5%+/ File: JOEL13.RD
12-APR-95 12:18
x10 2
6.80
6.12
5.44
4.76
4.08
3.40
2.72
2.04
1.36
0.68
2.20 (0.4803) 12.8%
2.70 (0.3439) 19.8% Mg3B2O6
3.60 (0.4586) 10.5% MgO
14.32
(1.8242)
7.85

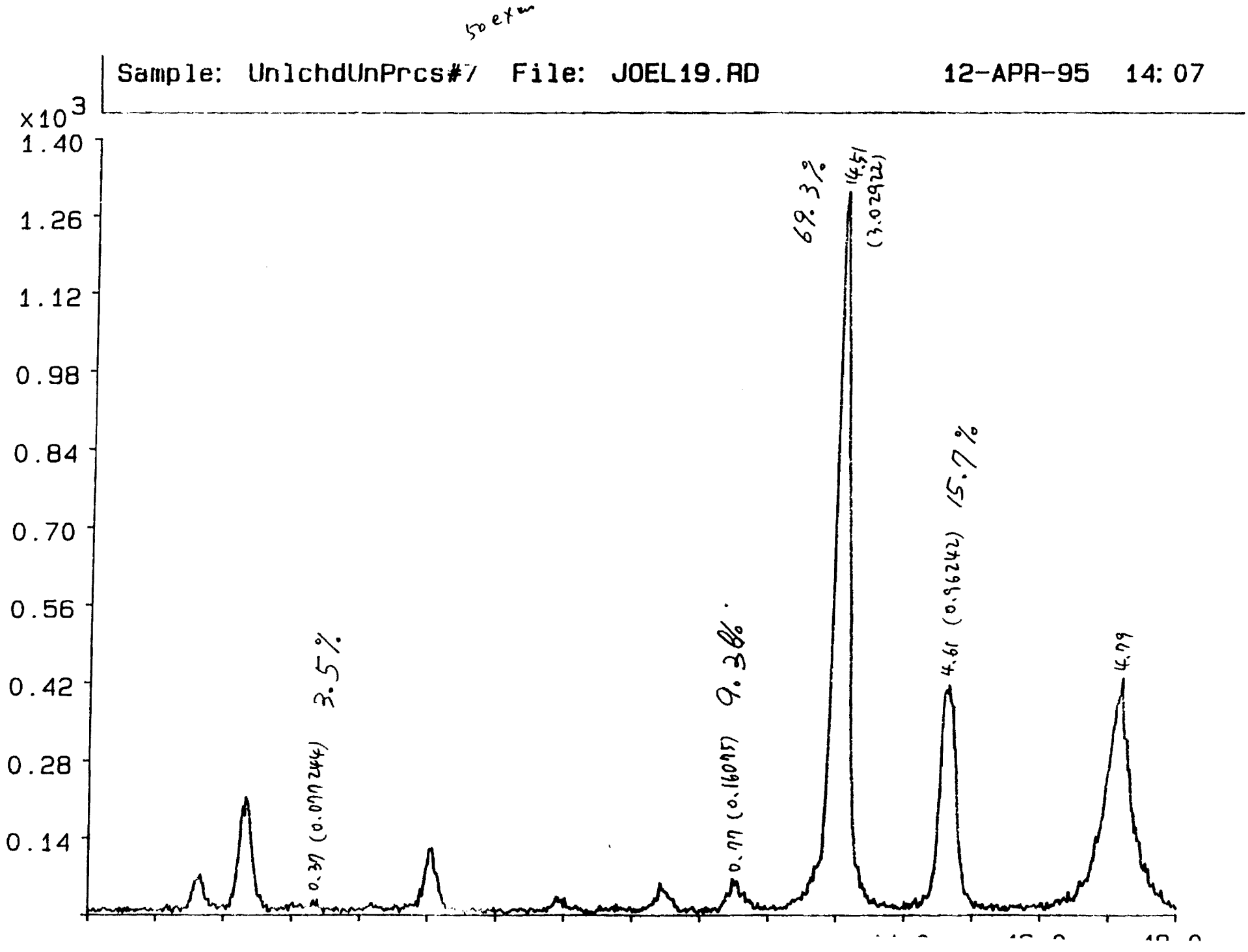

Sample: Leach1/5%/#2 File: JOEL14.RD 12-APR-95 12:29
x10 2
6.80
6.12
5.44
4.76
4.08
3.40
2.72
2.04
1.36
0.68
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
1.82 (0.1869) 8.5%
1.94 (0.1992) 11.5%
15.14 (1.5544) 35.6%
10.0 (1.0267) 16.8%
9.74

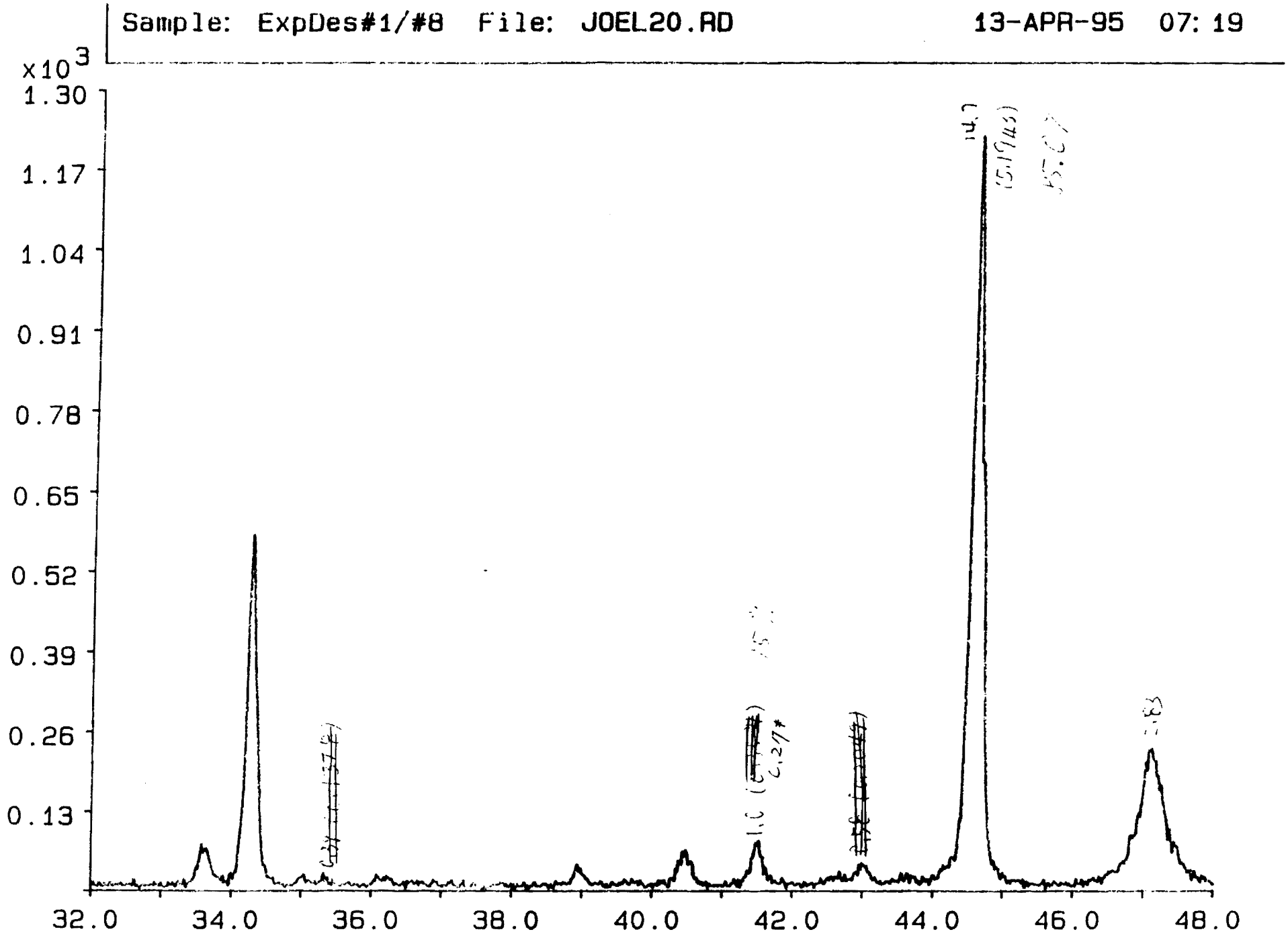

Sample: 1stLch/50%/#3 File: JOEL15.RD 12-APR-95 12:49
x10 2
7.80
7.02
6.24
5.46
4.68
3.90
3.12
2.34
1.56
0.78
0.62 (0.0706) 4.1 %
2.09 (0.3056) 17.6%
9.59 (1.4020) 32.1%
15.0 (2.1930) 35.9 %
6.84

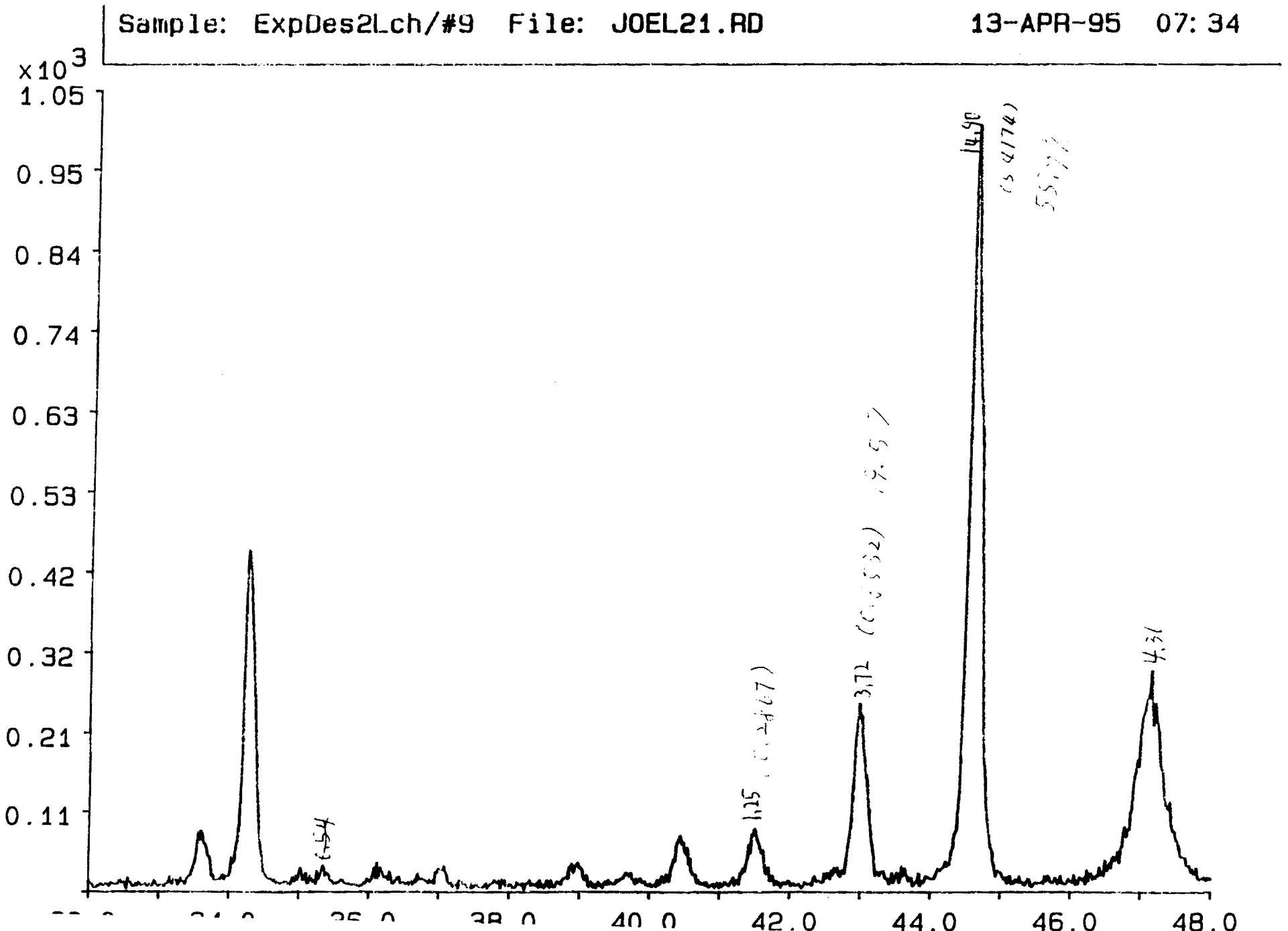

Sample: 2ndLch/5%/#4 File: JOEL16.RD 12-APR-95 13: 10
x10 2
6.80
6.12
5.44
4.76
4.08
3.40
2.72
2.04
1.36
0.68
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
2.69 (0.34844) 15.9%
2.58 (0.33419) 12.2%
2.71 (0.35103) 8.0%
13.62 (1.76424) 28.9%
7.02

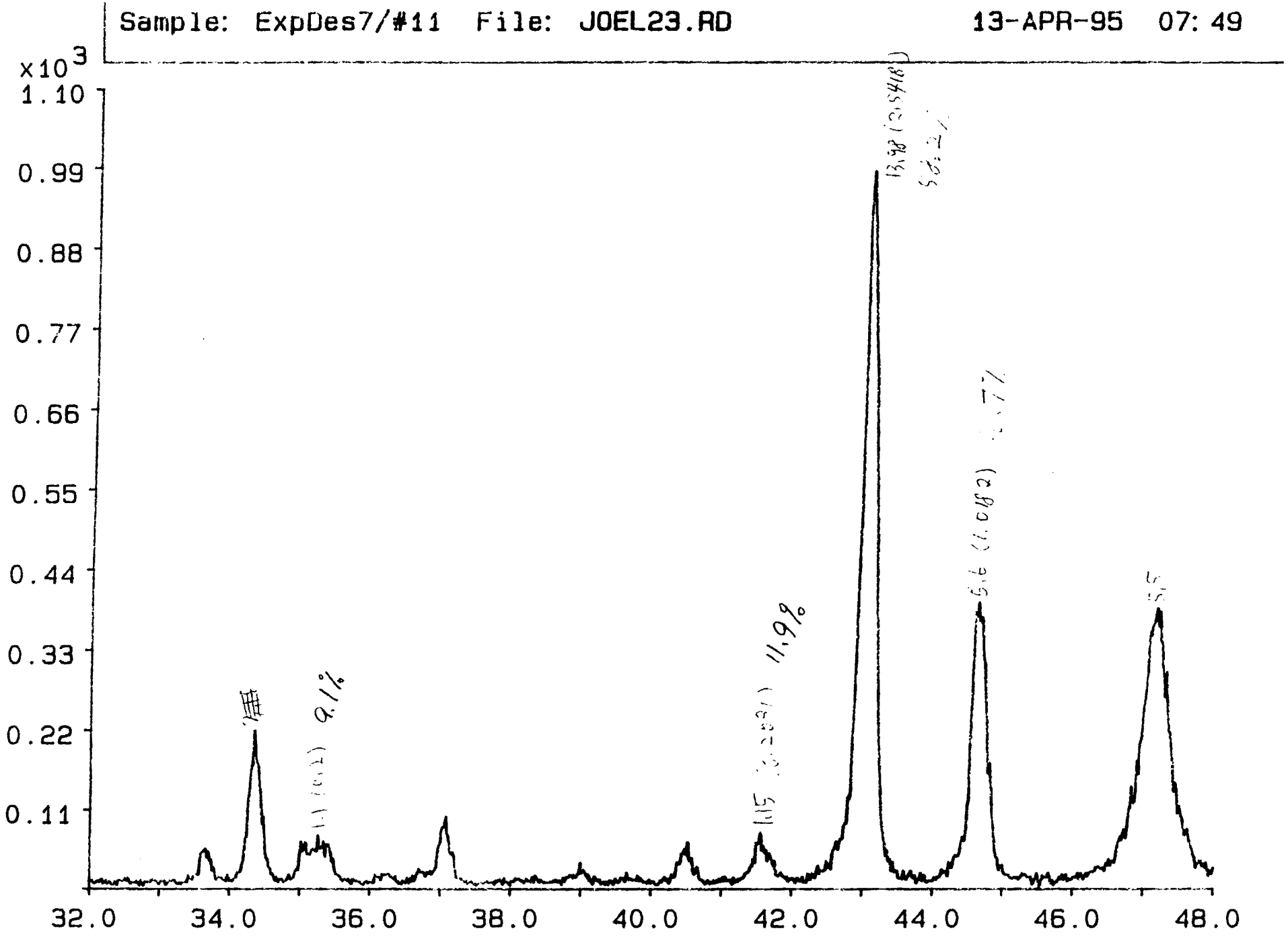

Sample: FnlPrd2ndSpl/#5 File: JOEL17.RD 12-APR-95 13:30
x10 2
9.50
8.55
7.60
6.65
5.70
4.75
3.80
2.85
1.90
0.95
1.20 (0.25) 11.4%
1.10 (0.292) 13.2%
0.85 (0.1191) 4.1%
15.45 (3.1582) 51.6%
4.8
46.0
48.0

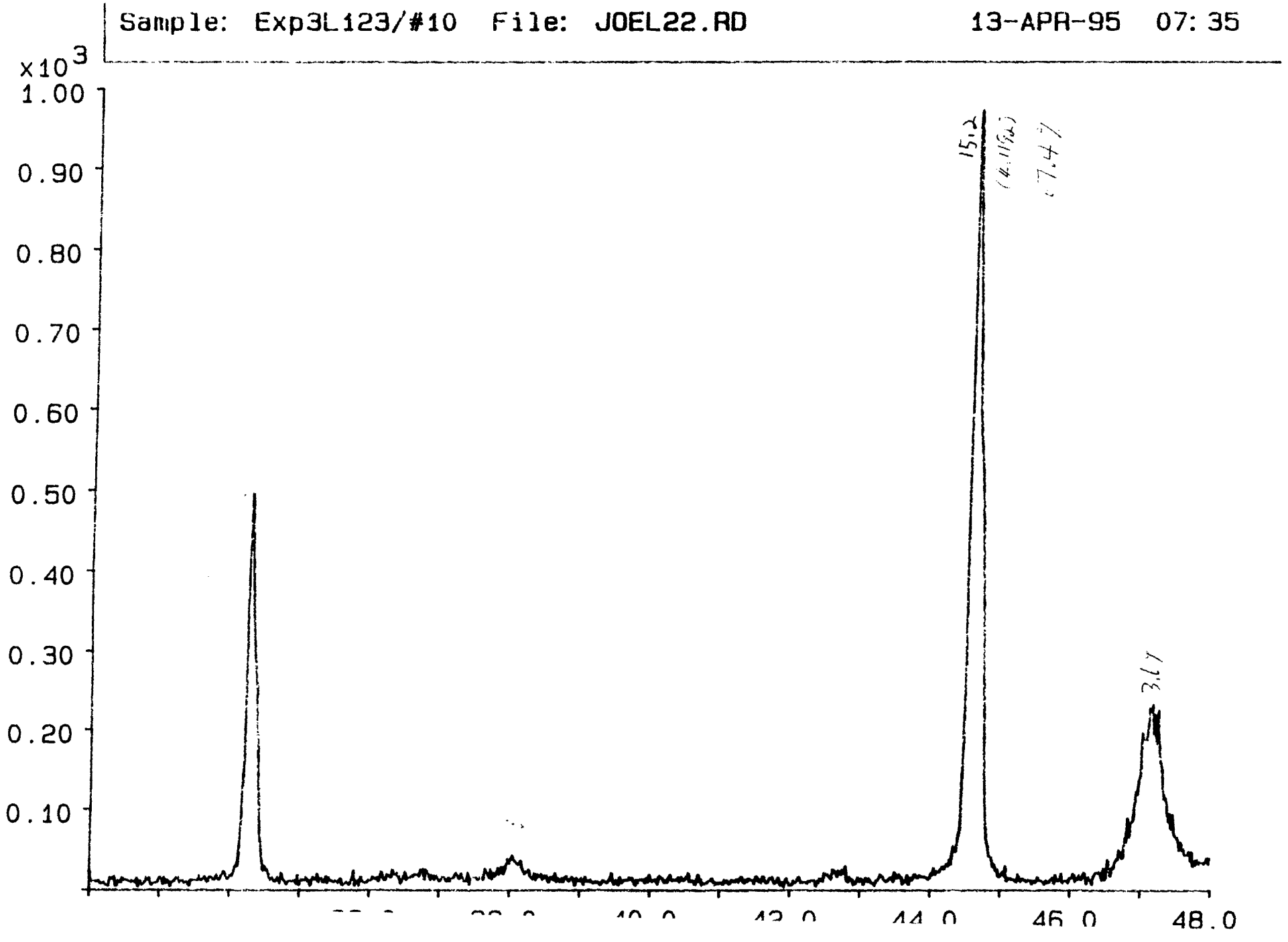

Sample: 5%Unlchd/#6 File: JOEL18.RD 12-APR-95 13:48
x10 2
9.00
8.10
7.20
6.30
5.40
4.50
3.60
2.70
1.80
0.90
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
7.6 %
42.8%
14.36
(1.86479)
12.5%
5.89 (0.96692)
7.68

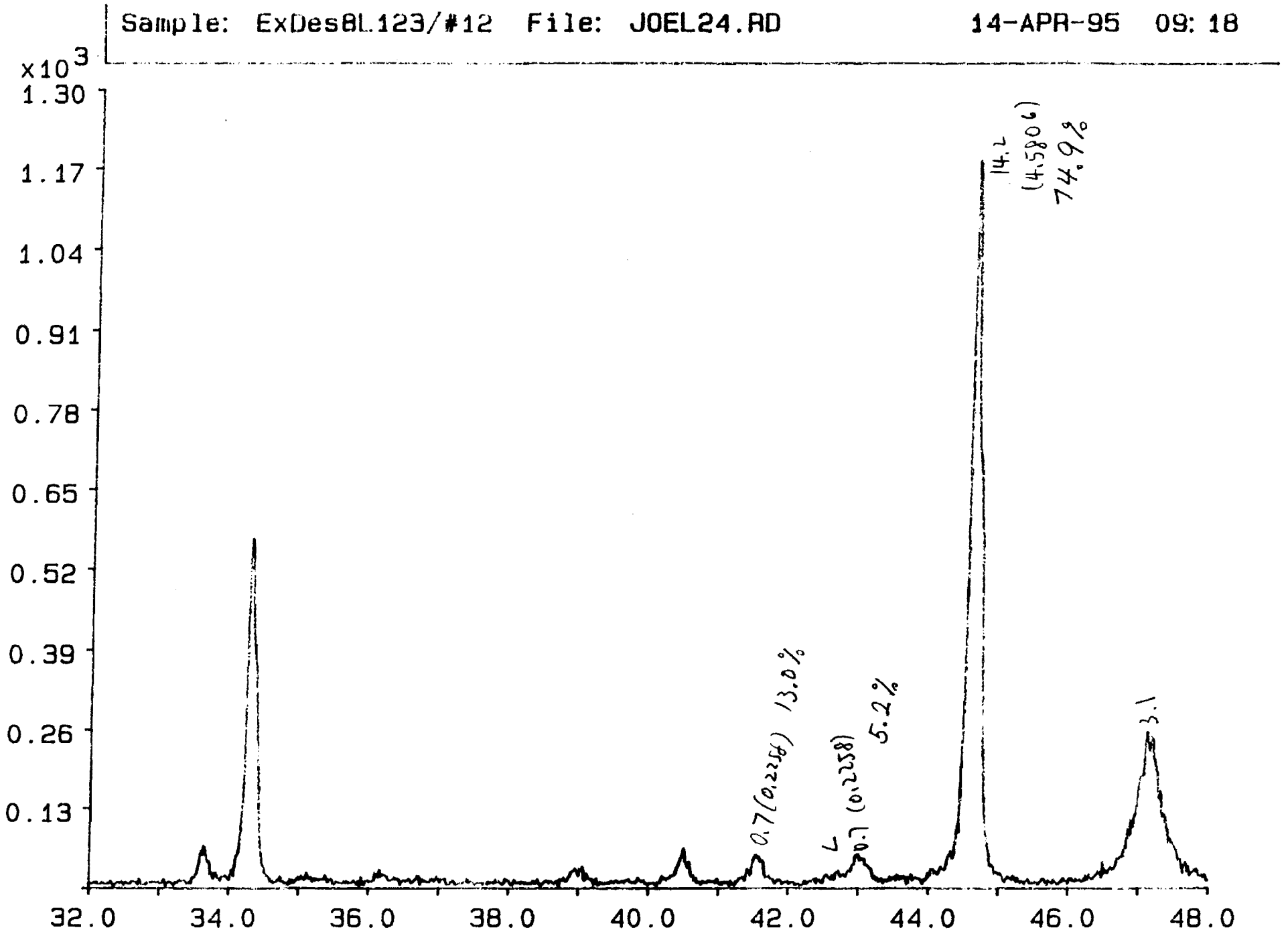

50 eter
Sample: UnlchdUnPrcs#7 File: JOEL19.RD 12-APR-95 14:07
x10 3
1.40
1.26
1.12
0.98
0.84
0.70
0.56
0.42
0.28
0.14
0.39 (0.011244)
3.5%
0.77 (0.16015)
9.3%
69.3%
14.51
(3.02922)
4.61 (0.96242)
15.7%
4.79

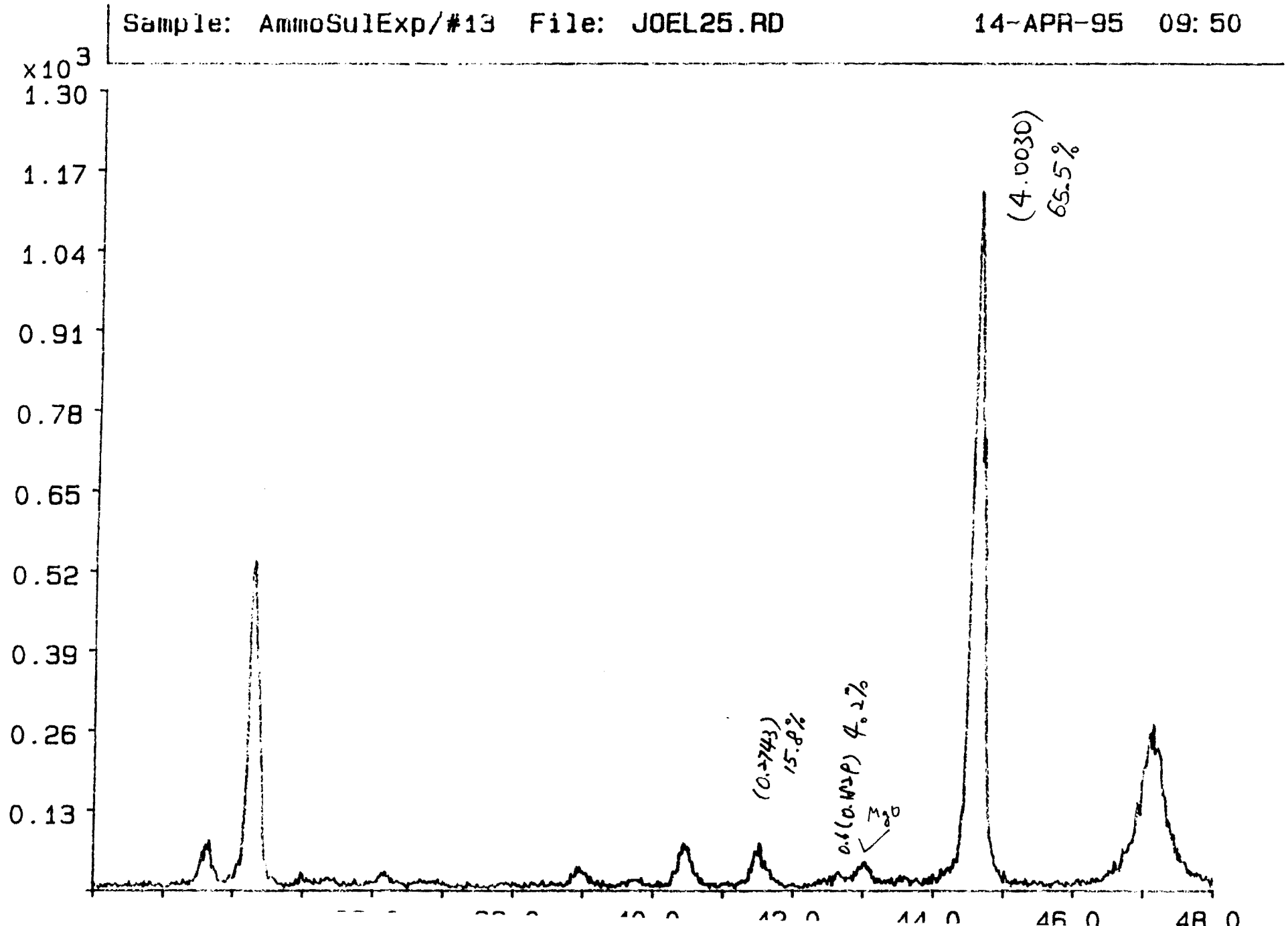

Sample: ExpDes#1/#8 File: JOEL20.RD 13-APR-95 07:19
x10^3
1.30
1.17
1.04
0.91
0.78
0.65
0.52
0.39
0.26
0.13
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0


Sample: ExpDes2Lch/#9 File: JOEL21.RD 13-APR-95 07:34
x10 3
1.05
0.95
0.84
0.74
0.63
0.53
0.42
0.32
0.21
0.11
4,31
40.0
42.0
44.0
46.0
48.0


Sample: ExpDes7/#11 File: JOEL23.RD 13-APR-95 07:49
x10 3
1.10
0.99
0.88
0.77
0.66
0.55
0.44
0.33
0.22
0.11
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0


Sample: Exp3L123/#10 File: JOEL22.RD
13-APR-95 07:35
x10 3
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
15.2
(4.11%)
: 7.47
3.17
46.0
48.0


Sample: ExDes8L123/#12 File: JOEL24.RD 14-APR-95 09:18
x10 3
1.30
1.17
1.04
0.91
0.78
0.65
0.52
0.39
0.26
0.13
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
14.2 (4.580°) 74.9%
0.7(0.225°) 13.0%
0.7 (0.225°)
5.2%
3.1


Sample: AmmoSulExp/#13 File: JOEL25.RD 14-APR-95 09:50
x10 3
1.30
1.17
1.04
0.91
0.78
0.65
0.52
0.39
0.26
0.13
(4.0030)
65.5%
(0.3743)
15.8%
0.4(0.4134) 4.2%
MgO

file:xrdq.aem

Effect of Reactant Batch Composition on the Products in SHS of TiB_2 by a Magnesium-Thermic Reduction

4-3-95

Hyunho Shin

School of Materials Science and Engineering,

Georgia Institute of Technology, Atlanta, GA 30332.

I Introduction

While SHS of TiB_2 by a magnesium-thermic reduction per the reaction

$$TiO_2 + B_2O_3 + 5Mg \rightarrow TiB_2 + 5MgO \quad (1)$$

is a reliable and an energy-efficient process, not all the batch is following reaction 1 as evident by the presence of byproducts such as $Mg_3B_2O_6$ and Mg_2TiO_4. It has also been speculated that appreciable gas phase has been formed during the reaction.[1] Hence it is necessary to get an optimal reactant batch composition for maximal yield of TiB_2. In order to characterize the relative weight percentage of product phase, a quantitative X-ray diffraction technique was used.

[1] H. Shin, V. Sundaram, and K.V. Logan, Reaction Sequence in Self-Propagating High Temperature Synthesis of TiB_2 by a Magnesium-Thermic Reduction, unpublished work.

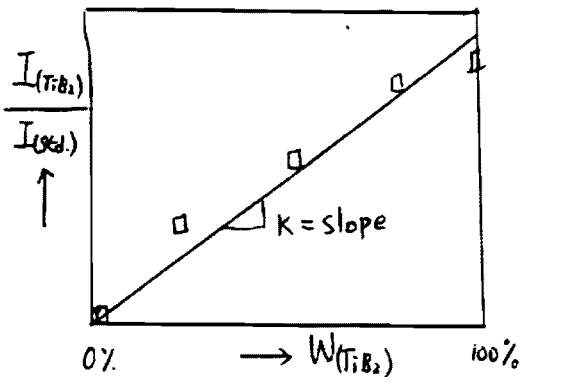
II Background of Quantitative X-ray Diffraction Technique

The reaction products contain different relative amounts of TiB_2, MgO, Mg_2TiO_4, and $Mg_3B_2O_6$. If we want to determine the amount of a certain phase, e.g., TiB_2, a diffraction line (in general primary peak) from TiB_2 is compared with a line from a standard substance mixed with the sample in known proportion. This is called internal standard method.

Suppose a known amount of original sample is mixed with a known amount of standard S to form a new composite sample. Then we obtain a diffraction pattern from the composite sample. The intensity ratio of a line from TiB_2 and a line from the standard S phase is a linear function of W_{TiB_2}, the weight fraction of TiB_2 in the original sample.

$$\frac{I_{TiB_2}}{I_{Std}} = k \cdot W_{TiB_2} \tag{2}$$

A calibration curve can be prepared from measurements on a set of synthetic samples with different compositions.



Once the calibration curve is established, the concentration of TiB_2 in an unknown sample is obtained simply by measuring the ratio $I_{TiB_2}/I_{Std.}$ for a composite sample containing the unknown and the same proportion of standard as was used in the calibration.

Notation	Cal#1	Cal#2	Cal#3	Cal#4	Cal#5
TiB_2	80	60	40	20	0
MgO	0	20	40	60	80
CaF2	20	20	20	20	20

Table 1: Composition of synthetic samples for the calibration of TiB_2 and MgO.

III Experimental Procedure

Out of searching diffraction patterns of more than 25 samples available in the lab, CaF2 was selected as the internal standard. This was because the primary peak intensity of CaF2 does not superimpose with any intensity lines of the four major phases in the reaction products. Furthermore it doesn't have many secondary peak intensities.

III.1 Calibration of TiB_2 and MgO

A set of synthetic samples with different compositions was prepared. The composition of each sample is shown in Table I. The synthetic samples named cal#1, cal#2, cal#3, cal#4, and cal#5, are corresponding to TiB_2 weight fraction of 100%, 75%, 50%, 25%, and 0% in original mixture (without CaF_2), repectively.

5 g batch each synthetic sample was thoroughfully mixed using mortar and pestle. XRD was performed using Cu K-α radiation with a step size of 0.02° and duration time of 1 sec

at each step.[2]

The commercially available TiB_2 and MgO were used for standard materials. The XRD patterns for Cal#1 - Cal#5 are shown in Figures 1-7. As shown in Figure 1, the commercially available TiB_2 has maximum peak intensity at $\sim 27.5°$ while standard reference sample has maximum intensity at $\sim 44°$. The commercially available TiB_2 is believed to have preferred orientation. Figure 2 shows the XRD pattern (Cal#1 sample) with different plotting scale. Figure 1 is drawn in a linear scale while Figure 2 is drawn in a square root scale. The peak height at 44° has been used for the TiB_2 calibration purpose while peak height at ~ 43 and $\sim 47°$ were used for the calibration of MgO and CaF_2, respectively. The calibration result is shown in Figures 8-9. Note that the composition is in terms of that in original mixture (without CaF_2).

III.2 Calibration of $Mg_3B_2O_6$

For $Mg_3B_2O_6$, powder mixture of $3MgO\text{-}B_2O_3$ was fired at 1200°C for 16 hrs in air. XRD pattern from this sample is shown in Figures 10-13 (with 20 wt% CaF_2). As shown in the figure, borate $Mg_3B_2O_6$ as well as $Mg_2B_2O_5$ is observed. In other words, the amount of MgO was insufficient in the mixture. The container of MgO powder was open and hence atmospheric water content might have contaminated the MgO mass, resulting in less MgO content in the weighed batch. The obtained $Mg_3B_2O_6$ was assumed to be ~ 55 wt%. This was based upon a ignition product sample ($3Mg\text{-}B_2O_3$-air) composed of MgO and $Mg_3B_2O_6$. This sample showed MgO weight percentage of 77.1, implying 22.9 wt.% of $Mg_3B_2O_6$. The

[2]Phillips, Model PW1800, Eindhoven, The Netherlands.

$I_{Mg_3B_2O_6}/I_{CaF_2}$ of this sample was 0.3977 as shown in Figure 14. This implies the slope K is equal to 0.3977/22.9 = 0.017367. Based upon this slope, a calibration curve is plotted in Figure 15.

III.3 Calibration of Mg_2TiO_4

2MgO-TiO_2 mixture was fired at 1610°C for 24 hrs. The result was Mg_2TiO_4 as well as $MgTiO_3$, implying the lack of MgO (MgO + $MgTiO_3$ = Mg_2TiO_4). XRD pattern from this material is shown in Figure 16. This material was simply assumed to be composed of 90 wt% Mg_2TiO_4. The XRD patterns used for Mg_2TiO_4 calibration curve is shown in Figures 17-19. The Mg_2TiO_4 calibration curve is shown in Figure 20.

III.4 XRD of Samples with Internal Standard

The original reaction products was also pulverized using mortar and pestle and then mixed with 20 wt% of CaF_2 internal standard (now they are composite samples) for the XRD characterization. The maximum peak height of the primary peak was used instead of the area under the curve for this method gives quick calculation with acceptable accuracy (JCPDS Alphabetical Search Manual). 12 X-ray diffraction patterns (with CaF_2 as internal standard) from different product batches are shown in Figures 21-32. Based upon these patterns, the intensity ratio of each phase with respect to CaF_2 is obtained. Then this ratio was used to obtain weight percentage of each phase in the reaction products.

IV Results

Sample	TiB_2	MgO	$Mg_3B_2O_6$	Mg_2TiO_4	glass
1T1M1B-O	9.7	46.8	11.3	11.2	21.0
1T1M5B-O	13.0	48.1	9.1	7.0	22.8
1T1M10B-O	14.3	45.7	10.3	7.6	22.1
1T5M5B-O	14.0	46.7	6.4	5.8	27.1
1T5M10B-O	14.8	50.7	7.7	5.9	20.9
1T10M10B-O	16.1	57.1	9.8	7.2	9.8
1T1M1B-Ar	14.7	54.3	5.9	9.1	16.0
1T1M5B-Ar	15.4	53.7	9.1	7.1	14.7
1T1M10B-Ar	14.3	45.2	7.6	10.9	22.0
1T5M5B-Ar	16.8	58.7	7.7	7.2	9.6
1T5M10B-Ar	15.5	51.7	7.9	7.4	17.5
1T10M10B-Ar	18.6	62.2	9.8	7.9	1.5

Table 2: Quantitative XRD result based upon the calibration curves.

Table 2 shows the weight percent of each phase using the calibration curves.

Appendix shows actual XRD patterns from the synthetic samples (used for the construction of the calibration curves) and from the composite samples (used to obtain the relative intensity of TiB_2 and MgO).

V Discussion

In general, reactions in argon result in more enhanced TiB_2 and MgO formation. Also the excess amount of Mg and B_2O_3 with same percentage ensured enhanced formation of TiB_2 (1M1B – 5M5B – 10M10B) both in air and argon. The MgO/TiB_2 weight ratio was less than ideal value of 2.899 especially when samples were reacted in air. This indicates that some portion of MgO is consumed for the formation of titanate (2mole MgO) and borate (3 mole MgO). Hence it is speculated that air reaction induces more titanates and borates. As far as excess amount of B_2O_3 enhances TiB_2 (diminishes borate) it is highly recommended to quantify the previously obtained reaction products with highly excessive B_2O_3 and Mg.

VI Summary

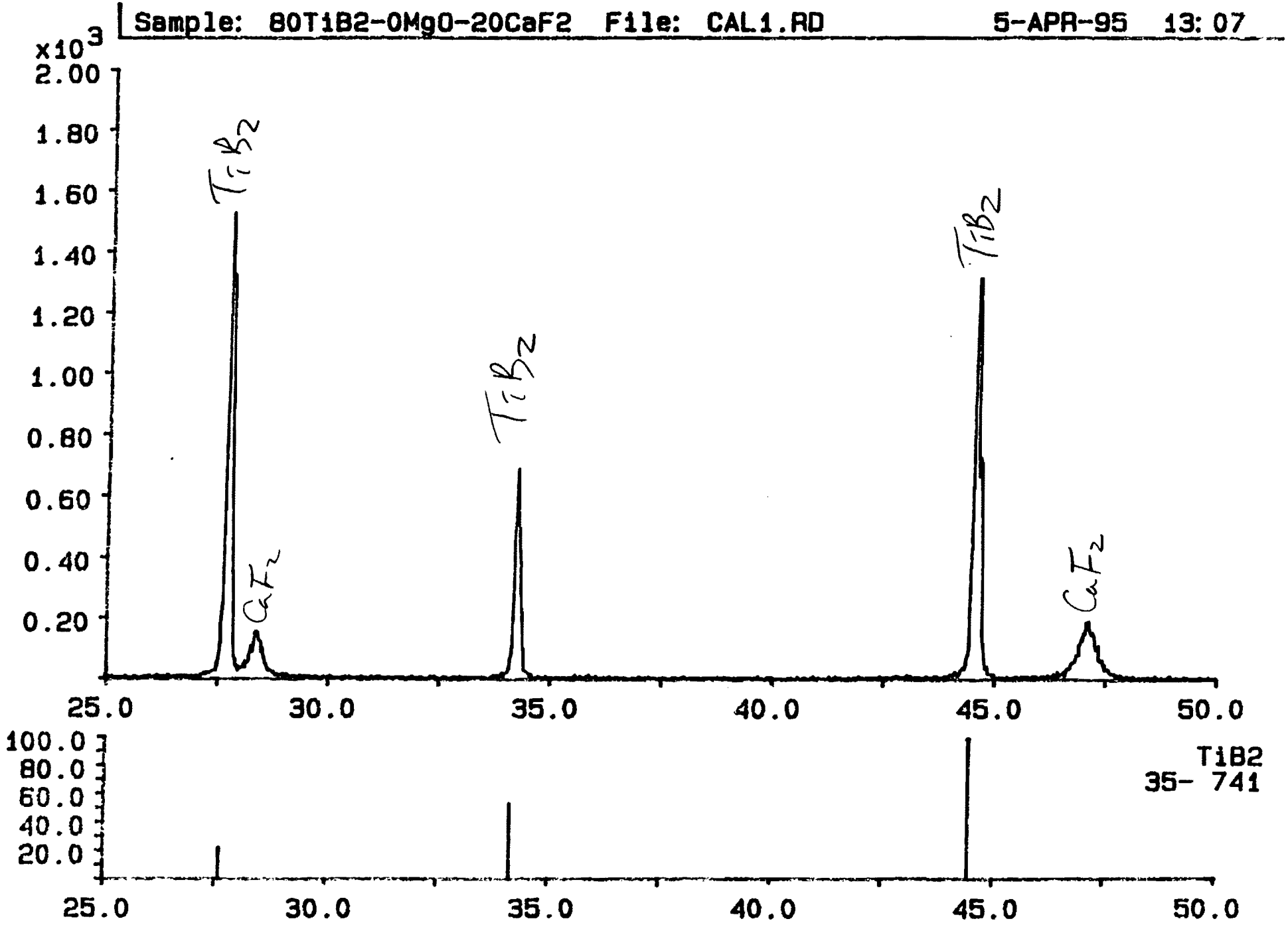
1. Reaction in argon produced more TiB_2 and MgO percentage with less probable glassy phase.
2. Excess amount of Mg and B_2O_3 with same percentage enhanced the formation of TiB_2.
3. Simple addition of B_2O_3 (1M1B $\rightarrow$ 1M5B $\rightarrow$ 1M10B) has a possibility of enhancing TiB_2 formation.

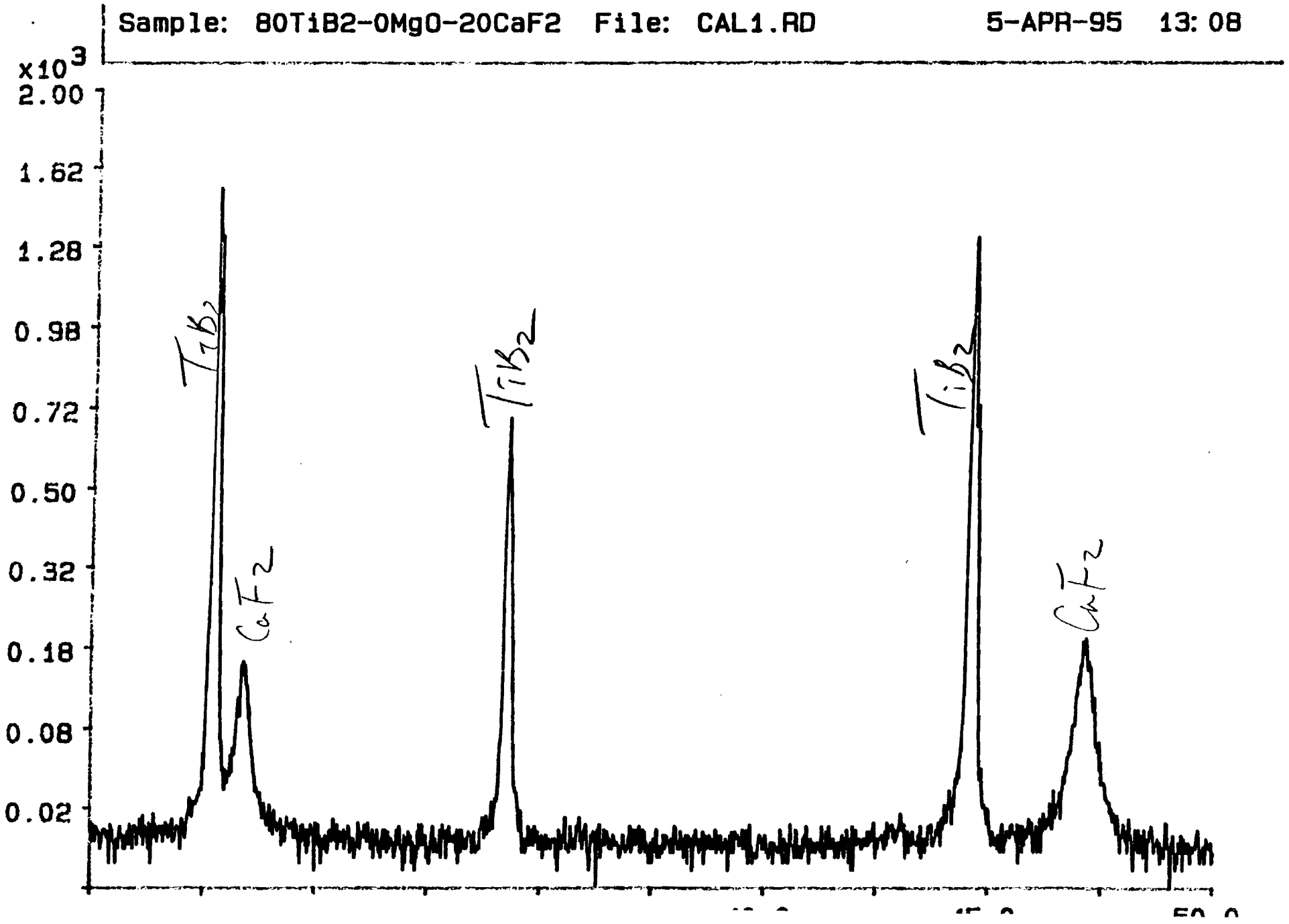
4. Argon reaction produced less borate and titanate.

5. Quantification of the previously obtained reaction products with different compositions is really worth while to do. This would provide a more enlarged view of the reaction.

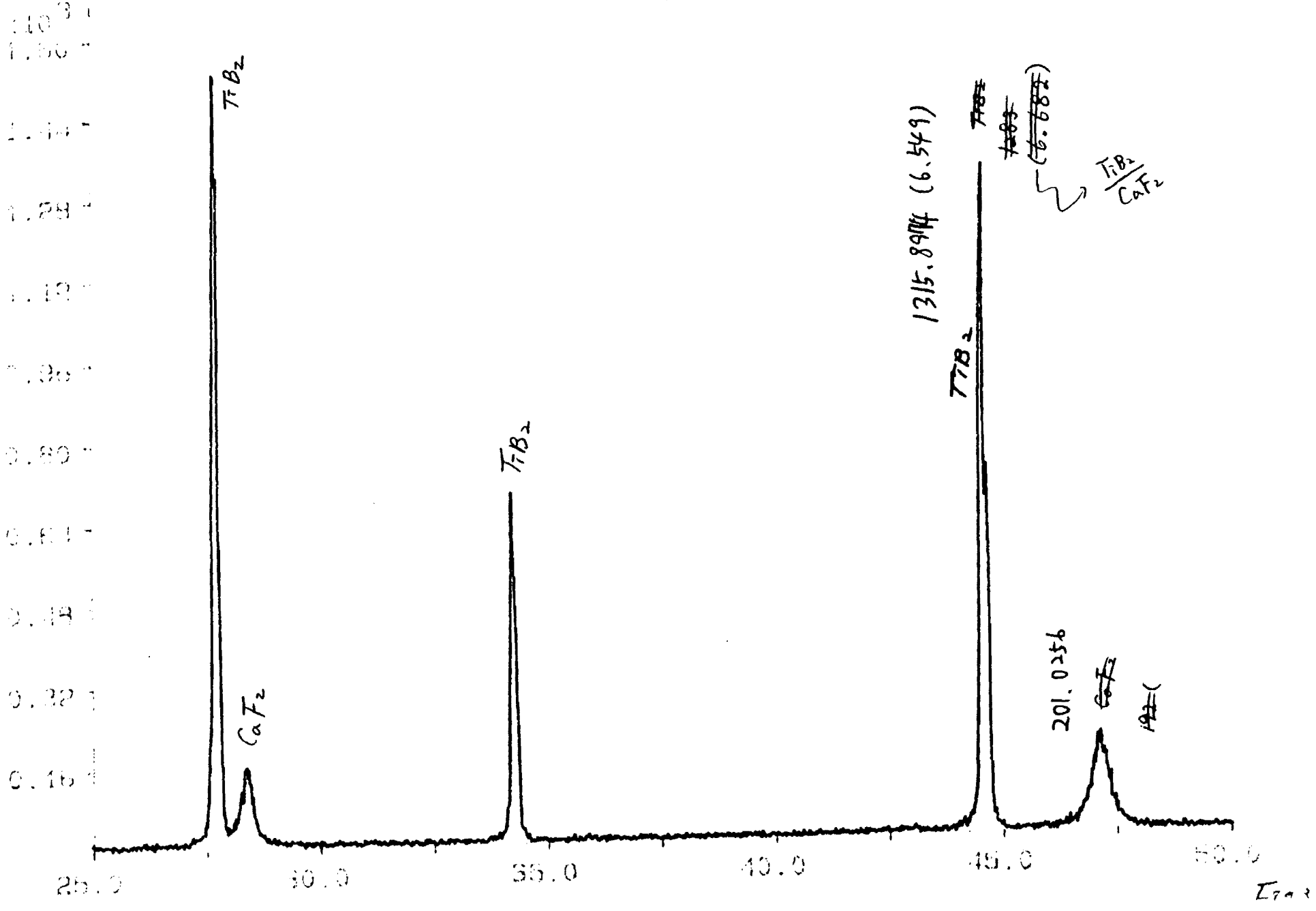
VII Remark

The standard sample for TiB_2 had preferred orientation so that the peak height at ~28° was higher than ~ 44° (Please refer to appendix Call.Rd diagram). The peak height at ~28° should be less than that at ~34°. If this standard sample had higher intensity only at ~28° (all other peaks were OK), then we are OK. If this standard sample had diminished peak intensity at ~44° than an ideal standard, we are overestimating TiB_2 weight percent. If the used standard sample had higher peak intensity values than an ideal standard, then we are underestimating the TiB_2 weight percent.

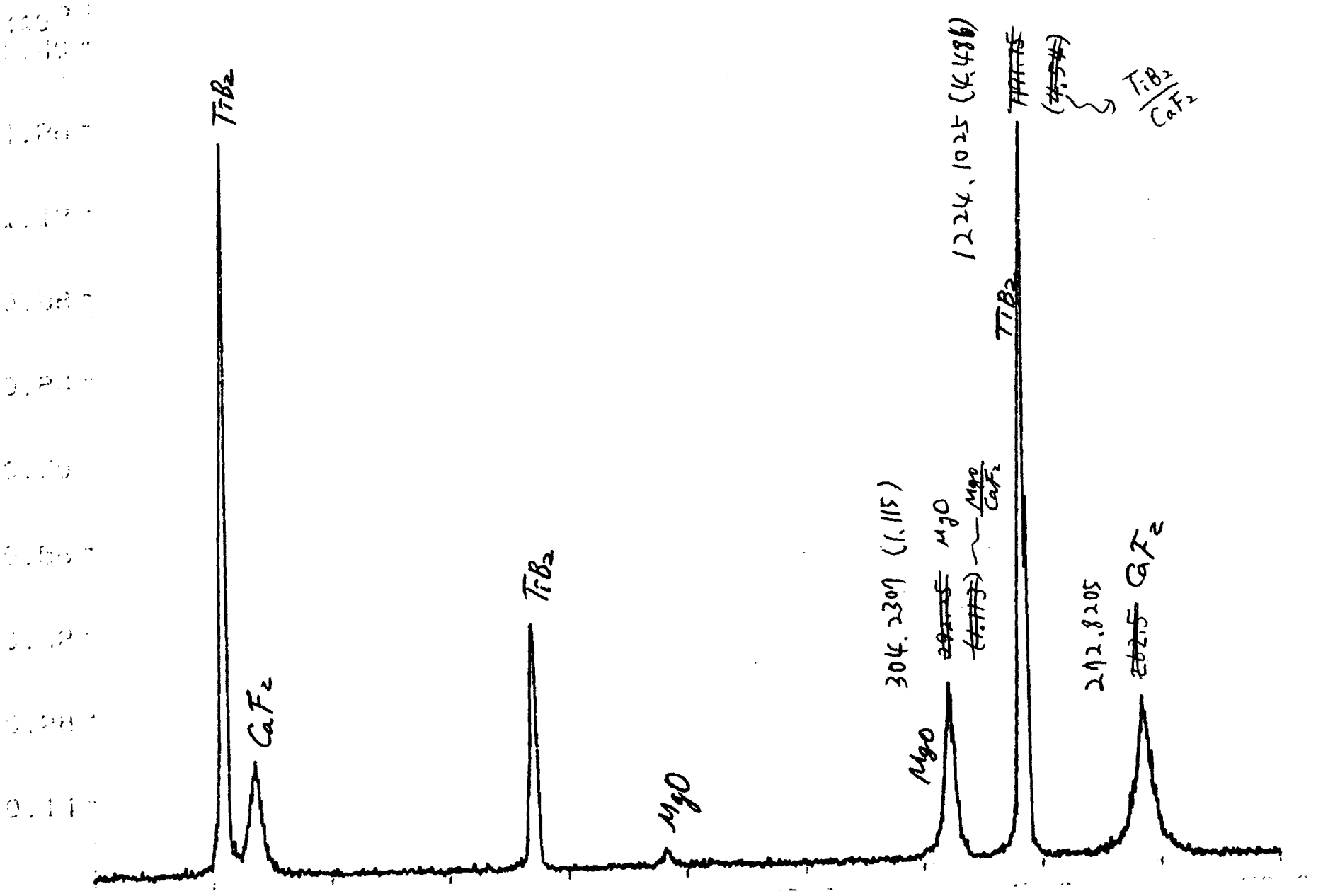

Sample: 80TiB2-0MgO-20CaF2 File: CAL1.RD 5-APR-95 13:07
x10 3
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
TiB2
CaF2
TiB2
TiB2
CaF2
25.0
30.0
35.0
40.0
45.0
50.0
100.0
80.0
60.0
40.0
20.0
TiB2
35- 741
25.0
30.0
35.0
40.0
45.0
50.0


Sample: 80TiB2-0MgO-20CaF2 File: CAL1.RD 5-APR-95 13:08
x10^3
2.00
1.62
1.28
0.98
0.72
0.50
0.32
0.18
0.08
0.02
TiB2
CaF2
TiB2
TiB2
CaF2

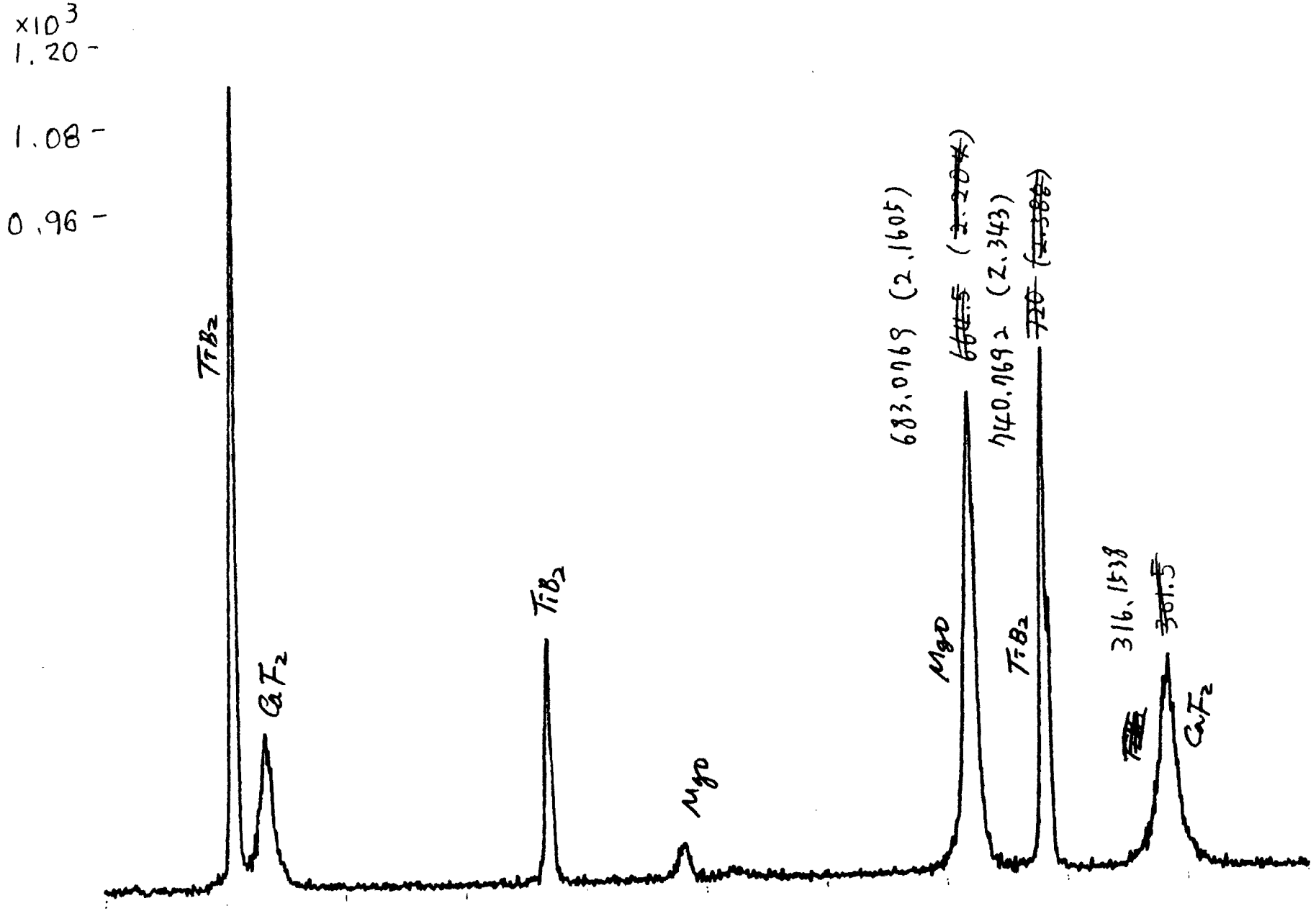
Sample: 80TiB2-0MgO-20CaF2 File: CAL1.RD 8-MAR-95 13: 46

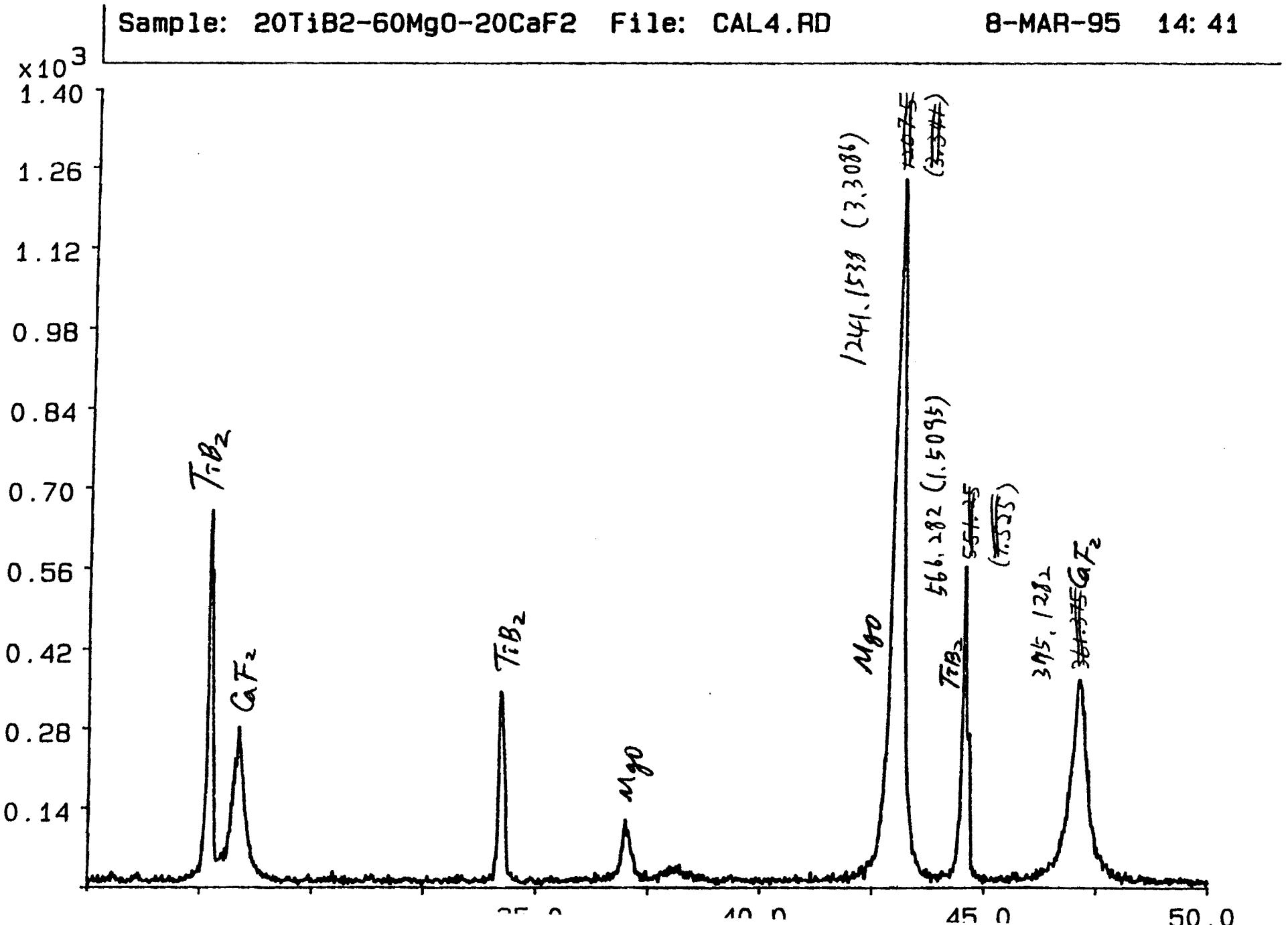


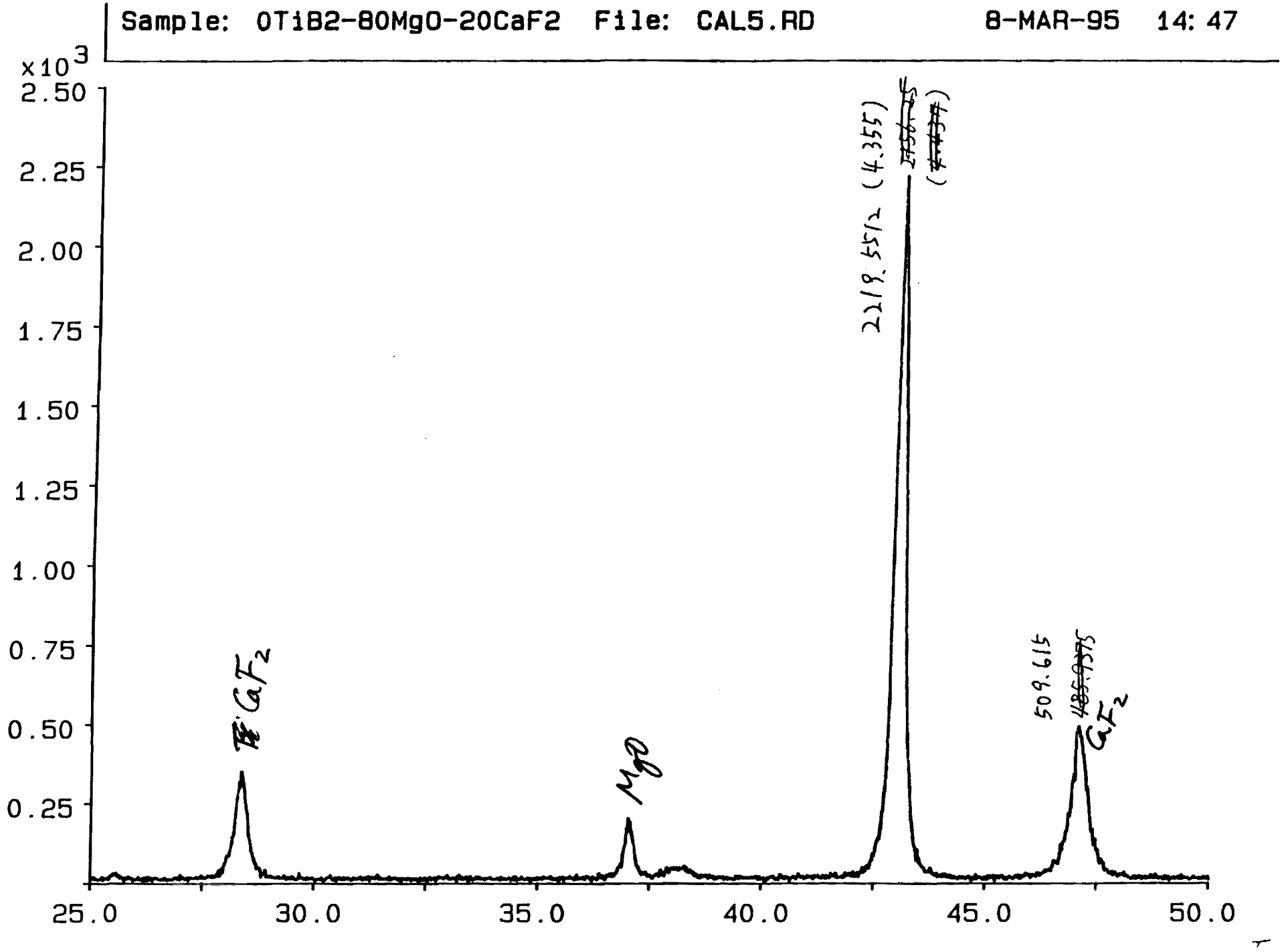
Sample: 60TiB2-20MgO-20CaF2 File: CAL2.RD 8-MAR-95 13:54



Sample: 40TiB2-40MgO-20CaF2 File: CAL3.RD 8-MAR-95 14:31




Sample: 20TiB2-60MgO-20CaF2 File: CAL4.RD 8-MAR-95 14:41
x10 3
1.40
1.26
1.12
0.98
0.84
0.70
0.56
0.42
0.28
0.14
TiB2
CaF2
TiB2
MgO
MgO
TiB2
CaF2
45.0
50.0


Sample: 0TiB2-80MgO-20CaF2 File: CAL5.RD 8-MAR-95 14:47
x10 3
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
25.0
30.0
35.0
40.0
45.0
50.0
CaF2
MgO
2219.5512 (4.355Å)
509.615
CaF2

Figure

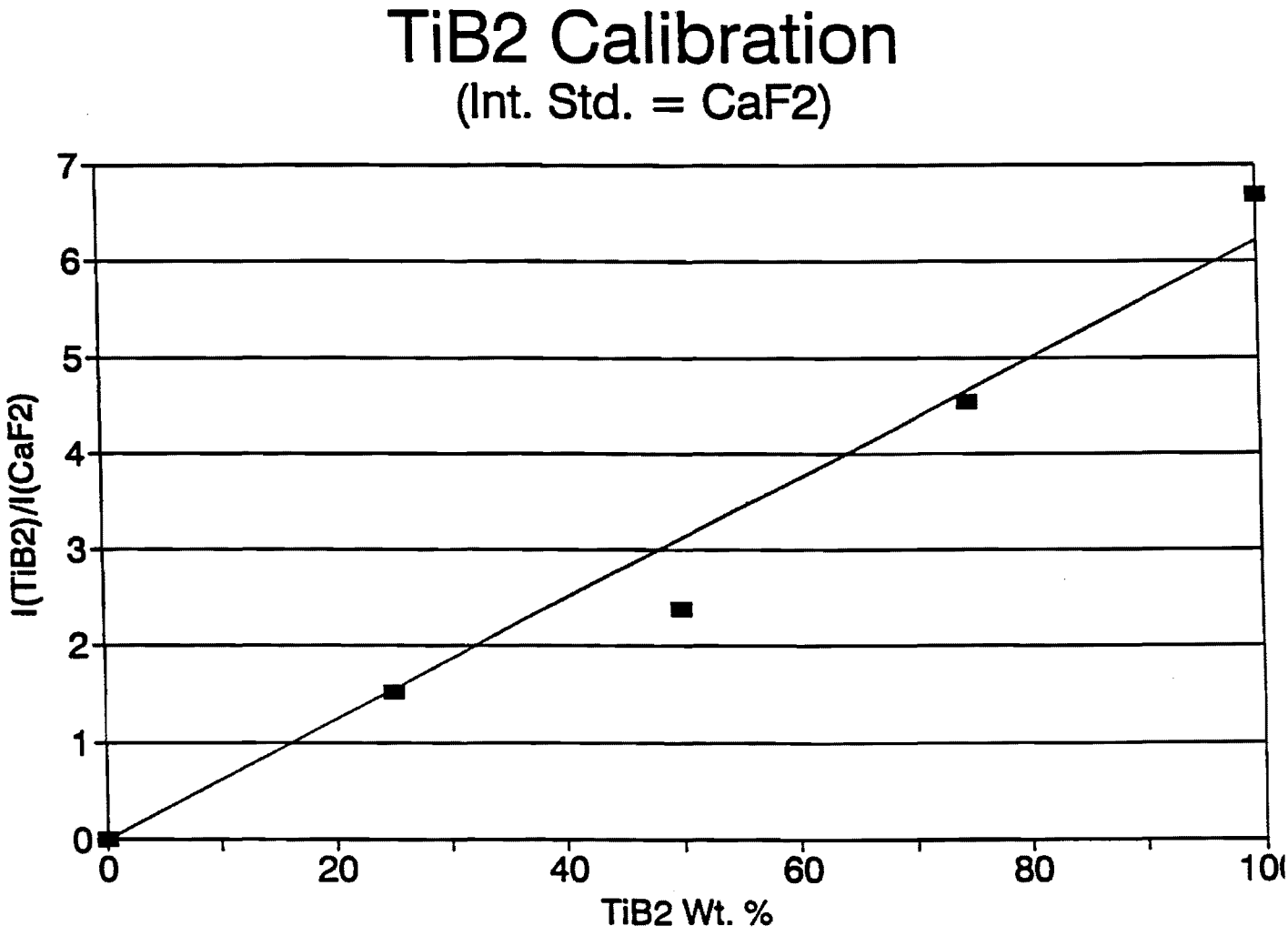
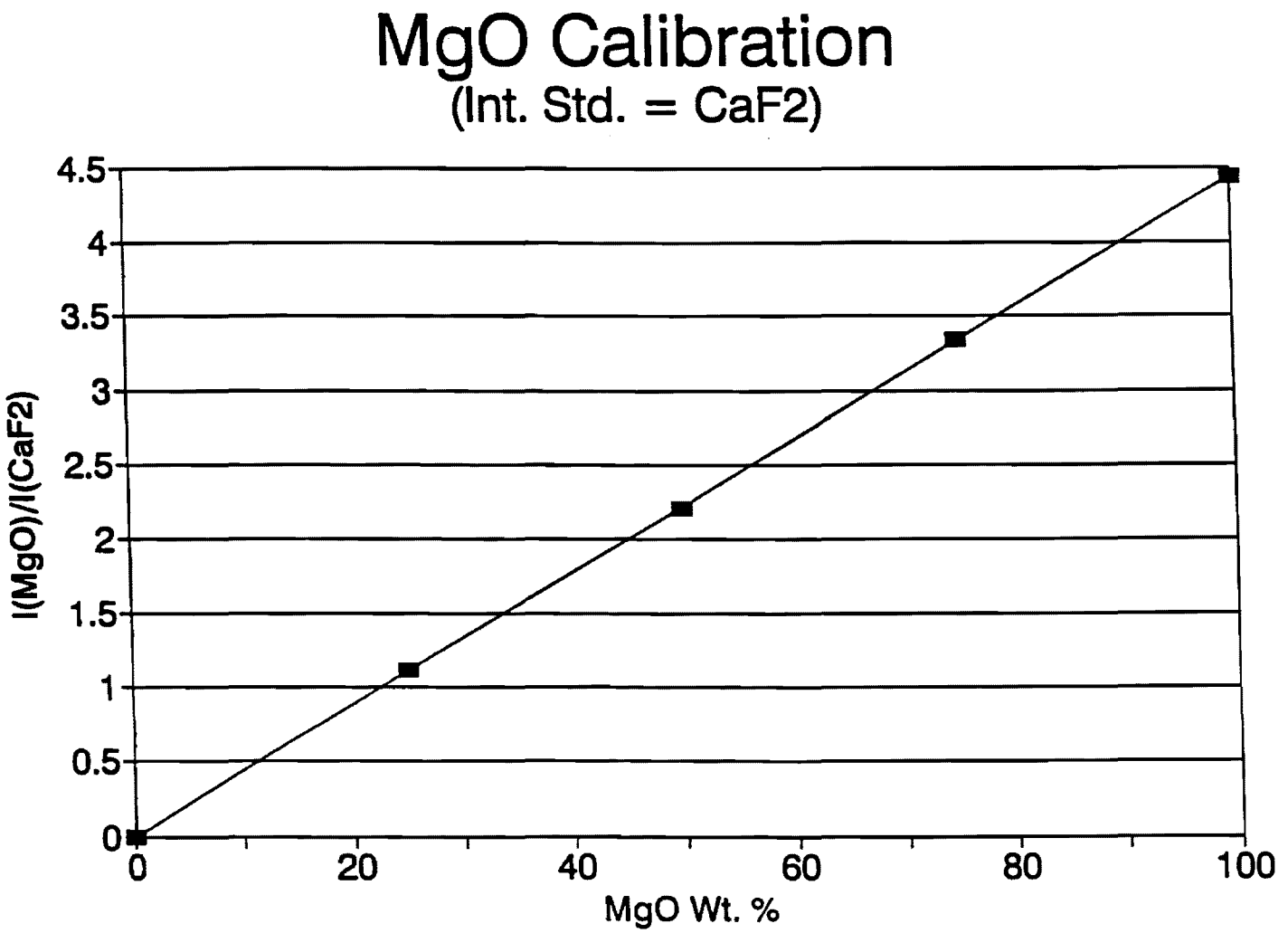
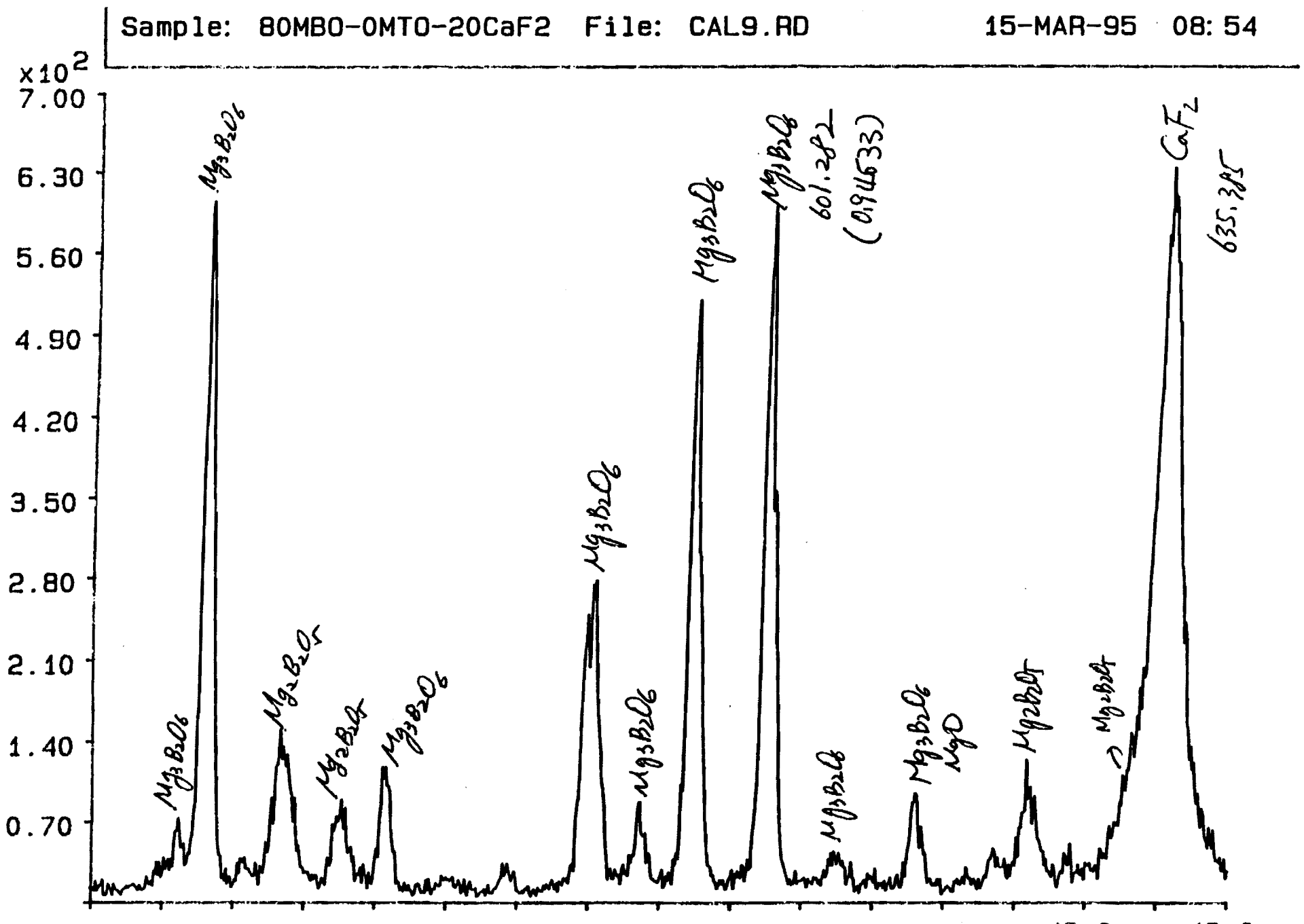

TiB2 Calibration
(Int. Std. = CaF2)
I(TiB2)/I(CaF2)
0
1
2
3
4
5
6
7
0
20
40
60
80
100
TiB2 Wt. %

Figure 2


MgO Calibration
(Int. Std. = CaF2)
I(MgO)/I(CaF2)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
20
40
60
80
100
MgO Wt. %


Sample: 80MBO-0MTO-20CaF2 File: CAL9.RD 15-MAR-95 08:54
x10 2
7.00
6.30
5.60
4.90
4.20
3.50
2.80
2.10
1.40
0.70
Mg3B2O6
Mg2B2O5
Mg2B2O5
Mg3B2O6
Mg3B2O6
Mg3B2O6
Mg3B2O6
Mg3B2O6
601.2θ2
(0.9465 33)
Mg3B2O6
Mg3B2O6
MgO
Mg2B2O5
Mg2B2O5
CaF2
635.385

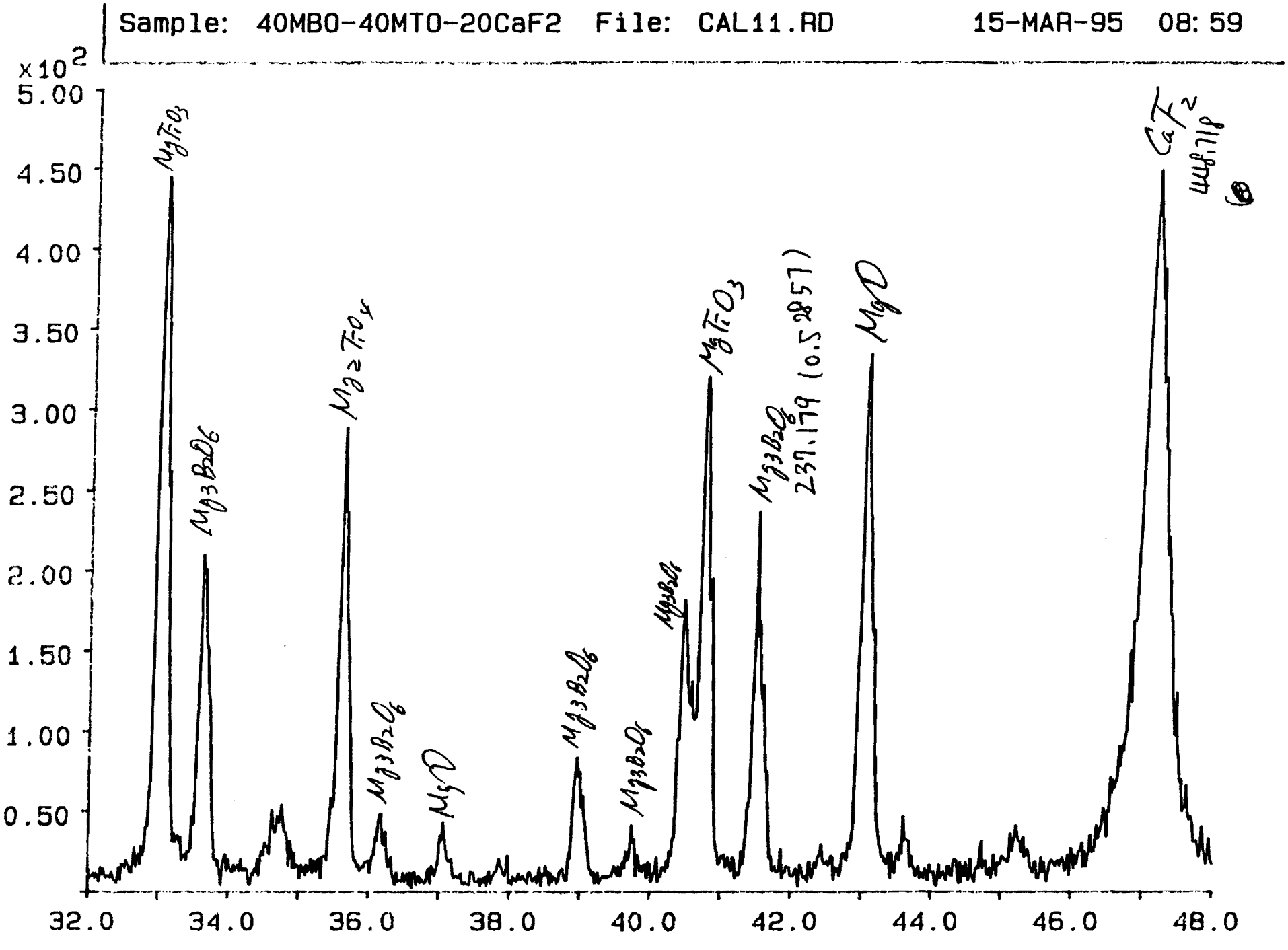
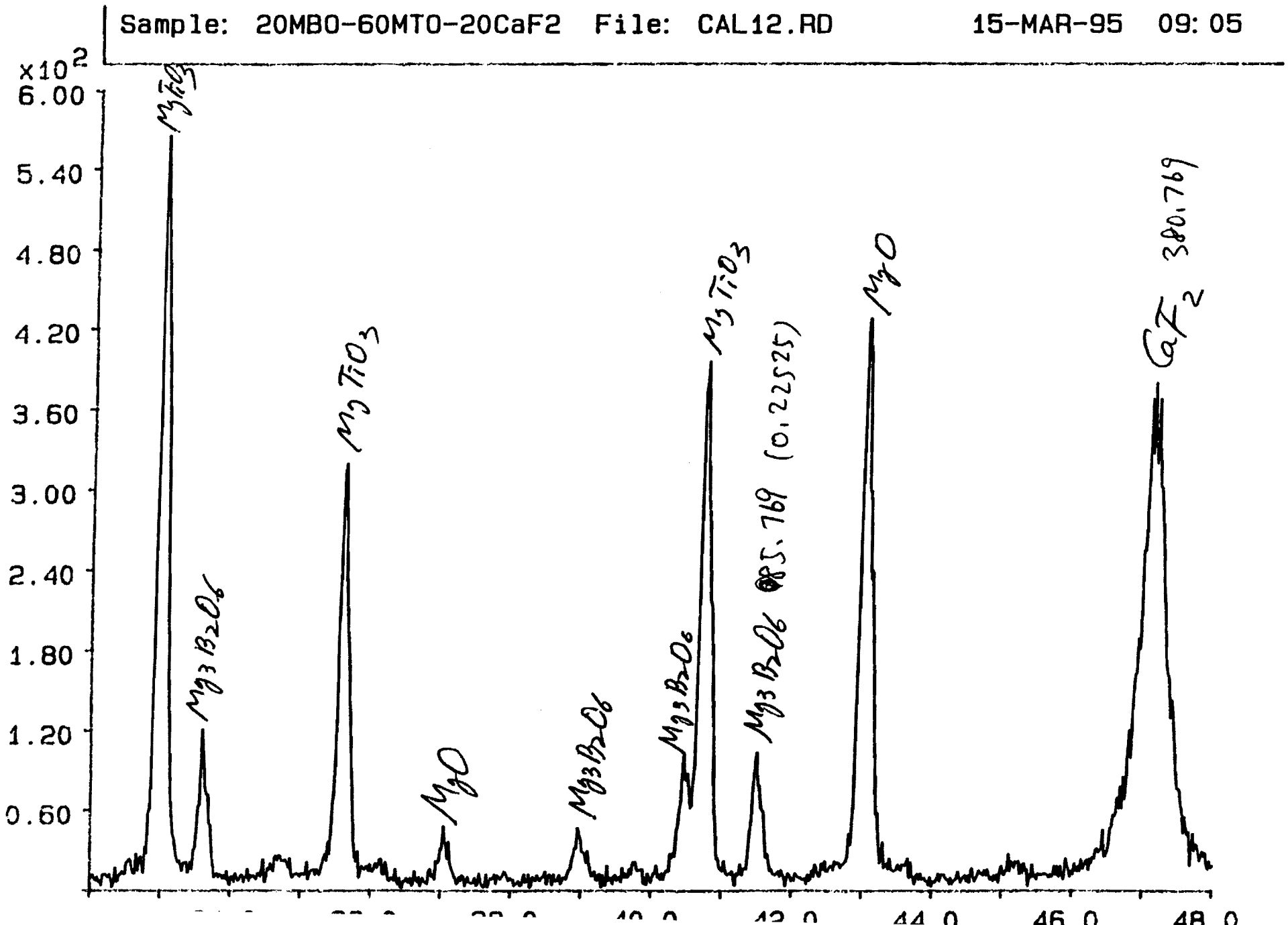
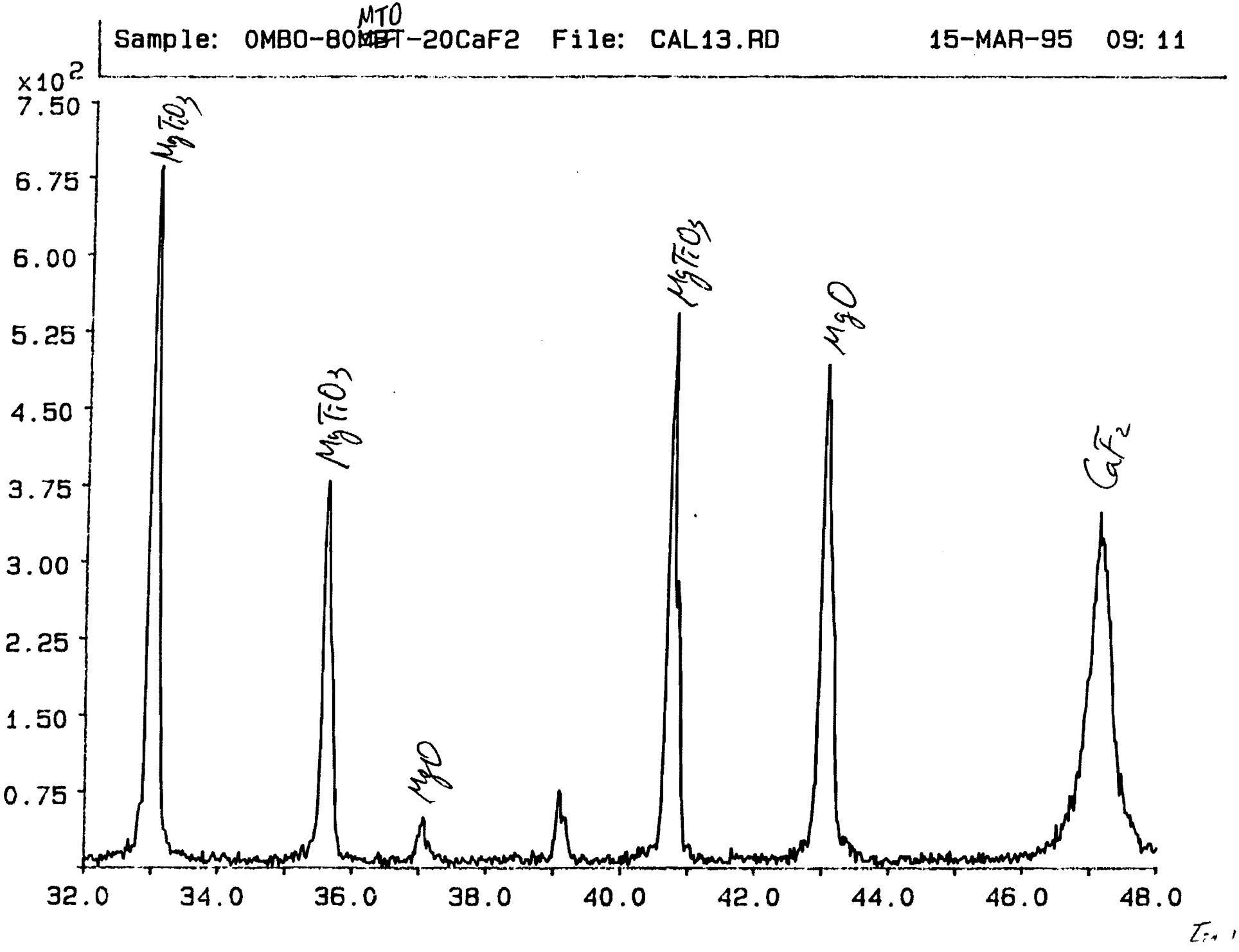
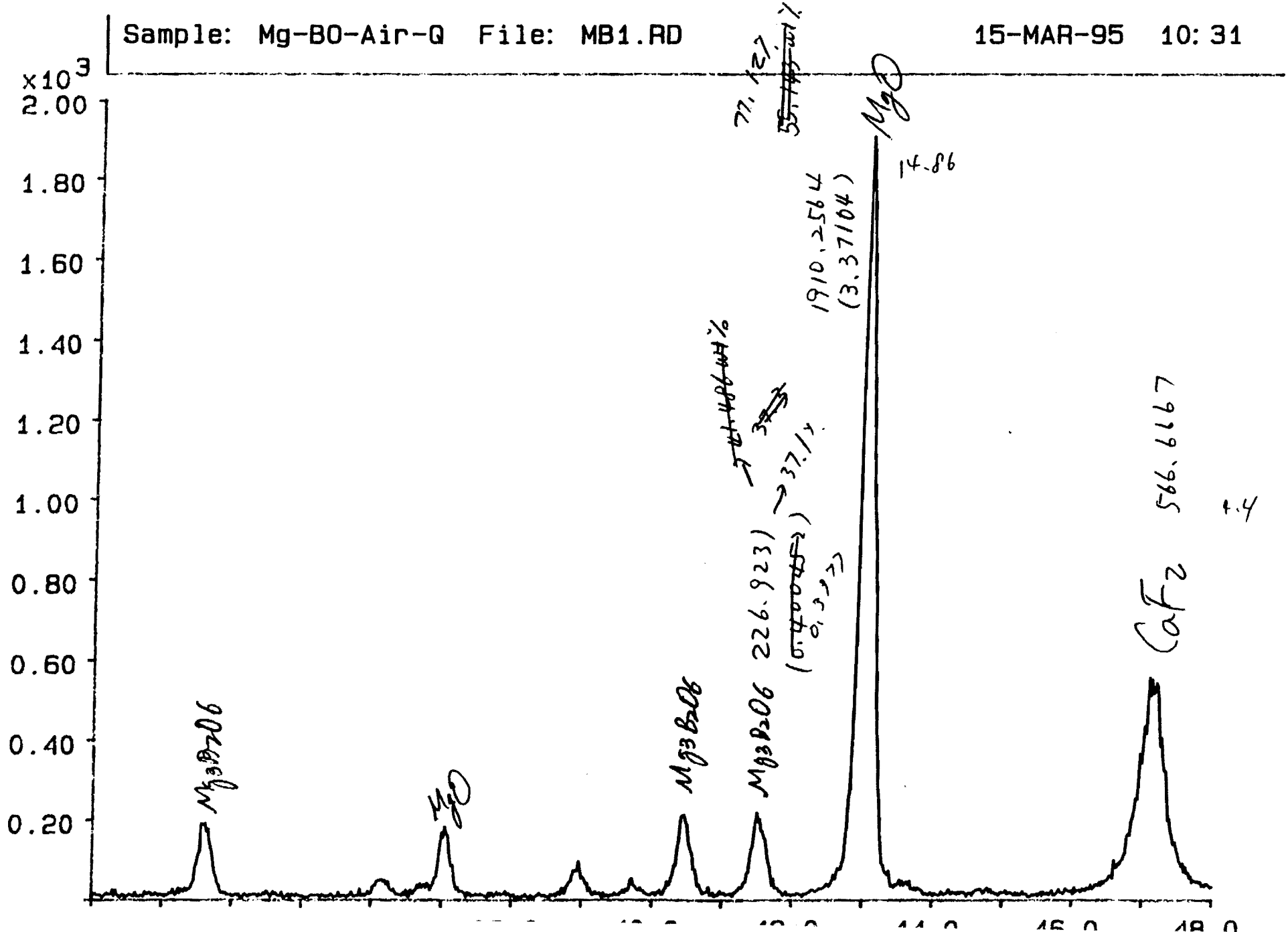
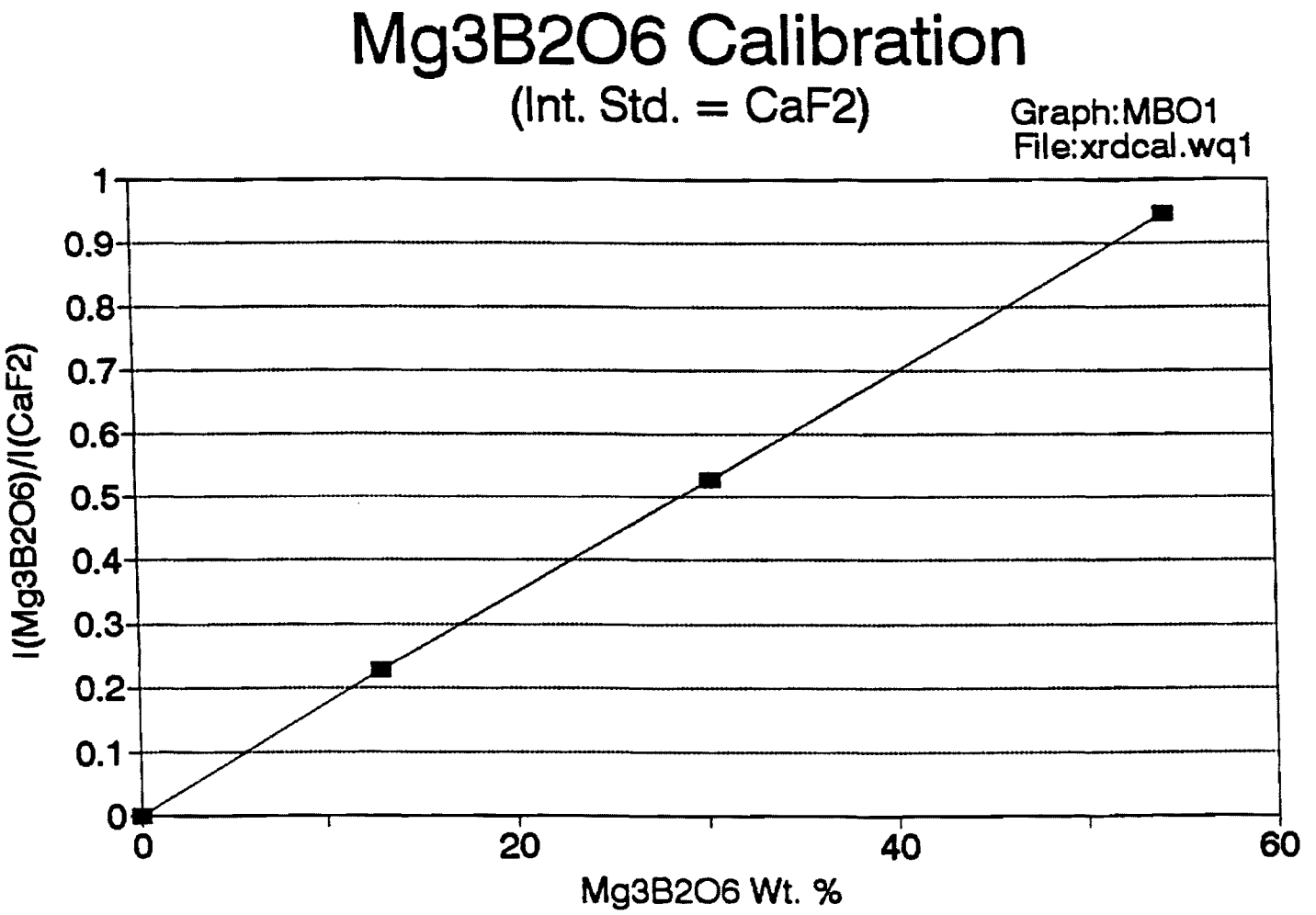

Sample: 40MBO-40MTO-20CaF2 File: CAL11.RD 15-MAR-95 08:59
x10 2
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
MgTiO3
Mg3B2O6
Mg2TiO4
Mg3B2O6
MgO
Mg3B2O6
Mg3B2O6
MgTiO3
Mg3B2O6
237.179 (0.52857)
MgO
CaF2
111.118

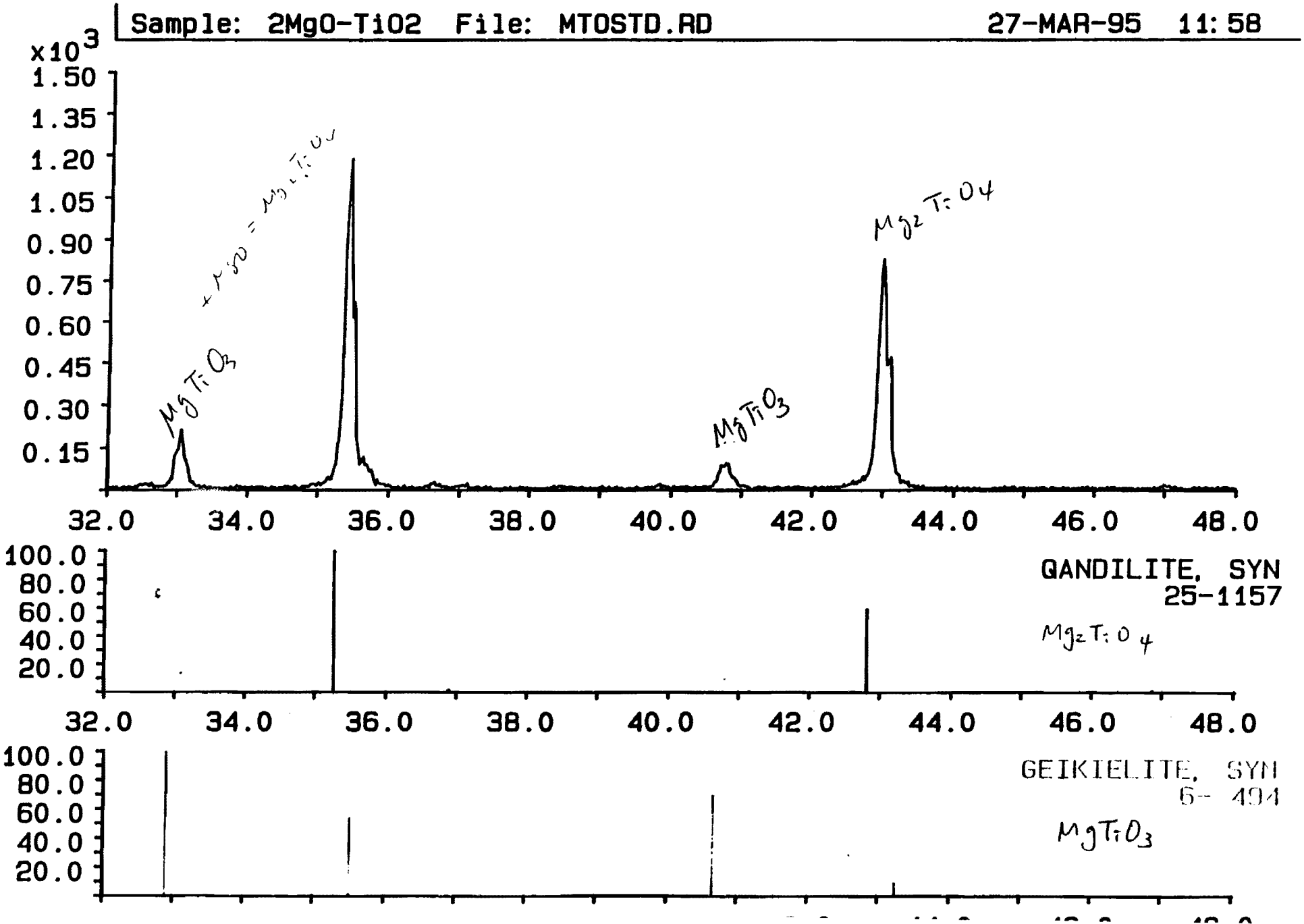
Fig 11


Sample: 20MBO-60MTO-20CaF2 File: CAL12.RD 15-MAR-95 09:05
x10 2
6.00
5.40
4.80
4.20
3.60
3.00
2.40
1.80
1.20
0.60
Mg3B2O6
MgTiO3
MgO
Mg3B2O6
Mg3B2O6
MgTiO3
Mg3B2O6 @35.769 (0.22525)
MgO
CaF2 38.769
44.0
46.0
48.0


Sample: 0MBO-80MTO-20CaF2 File: CAL13.RD 15-MAR-95 09:11
x10^2
7.50
6.75
6.00
5.25
4.50
3.75
3.00
2.25
1.50
0.75
MgTiO3
MgTiO3
MgO
MgTiO3
MgO
CaF2
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0


Sample: Mg-BO-Air-Q File: MB1.RD
15-MAR-95 10:31
x10 3
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
MgO
14.86
1910.25647
(3.37104)
226.923
(0.40045)
37.12
CaF2
586.6667
4.4


Mg3B2O6 Calibration
(Int. Std. = CaF2)
Graph:MBO1
File:xrdcal.wq1
I(Mg3B2O6)/I(CaF2)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
Mg3B2O6 Wt. %


Sample: 2MgO-TiO2 File: MTOSTD.RD 27-MAR-95 11:58
x10^3
1.50
1.35
1.20
1.05
0.90
0.75
0.60
0.45
0.30
0.15
MgTiO3 + Mg2TiO4 = Mg2Ti2O5
MgTiO3
Mg2TiO4
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
100.0
80.0
60.0
40.0
20.0
QANDILITE, SYN
25-1157
Mg2TiO4
GEIKIELITE, SYN
6- 494
MgTiO3

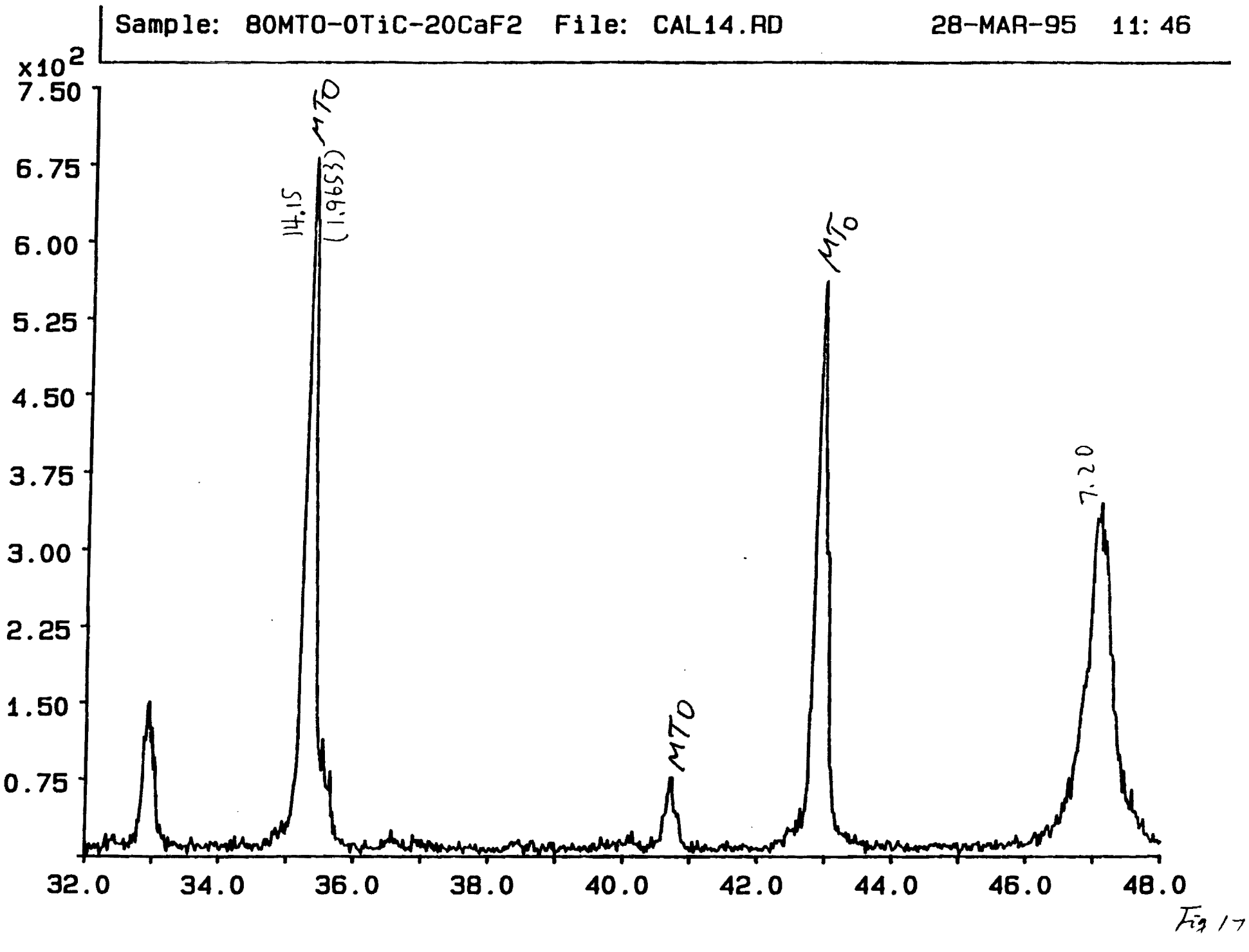
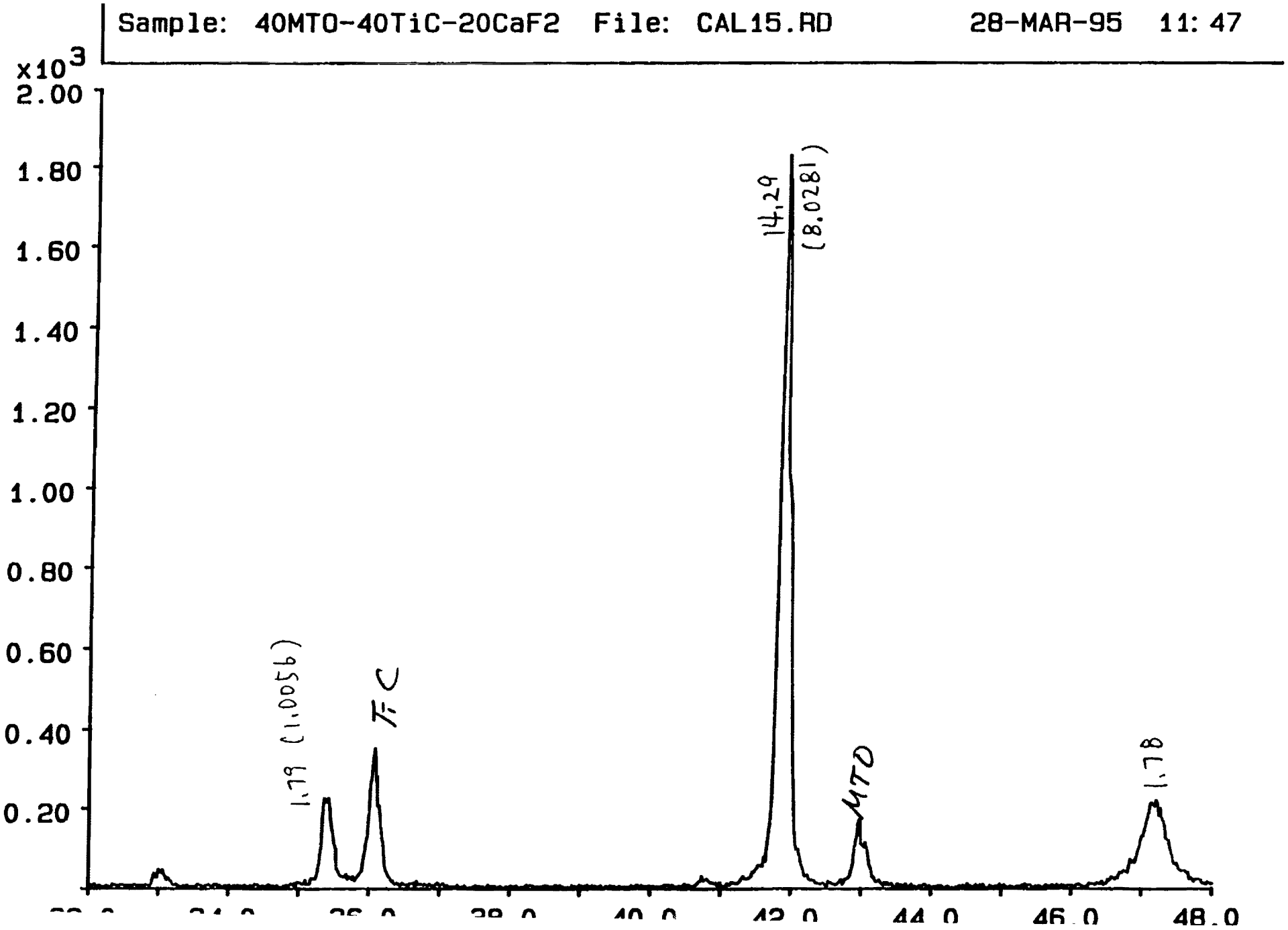

Sample: 80MTO-0TiC-20CaF2 File: CAL14.RD 28-MAR-95 11:46
x10^2
7.50
6.75
6.00
5.25
4.50
3.75
3.00
2.25
1.50
0.75
14.15
(1.9653)
MTO
MTO
MTO
7.20
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0

Fig 17


Sample: 40MTO-40TiC-20CaF2 File: CAL15.RD 28-MAR-95 11:47
x10^3
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
1.79 (1.0056)
TiC
14.29
(8.0281)
MTO
1.78
44.0
46.0
48.0

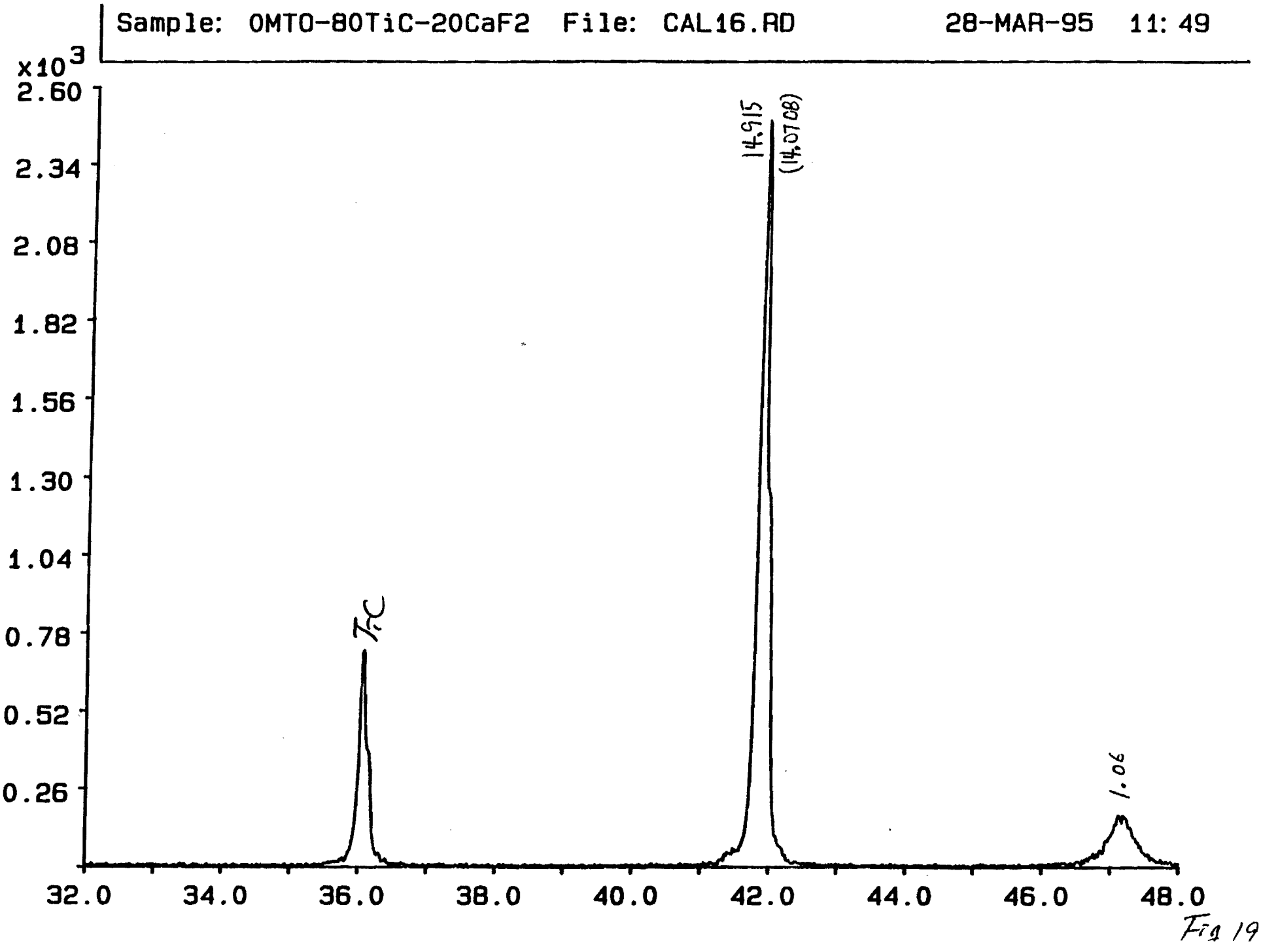
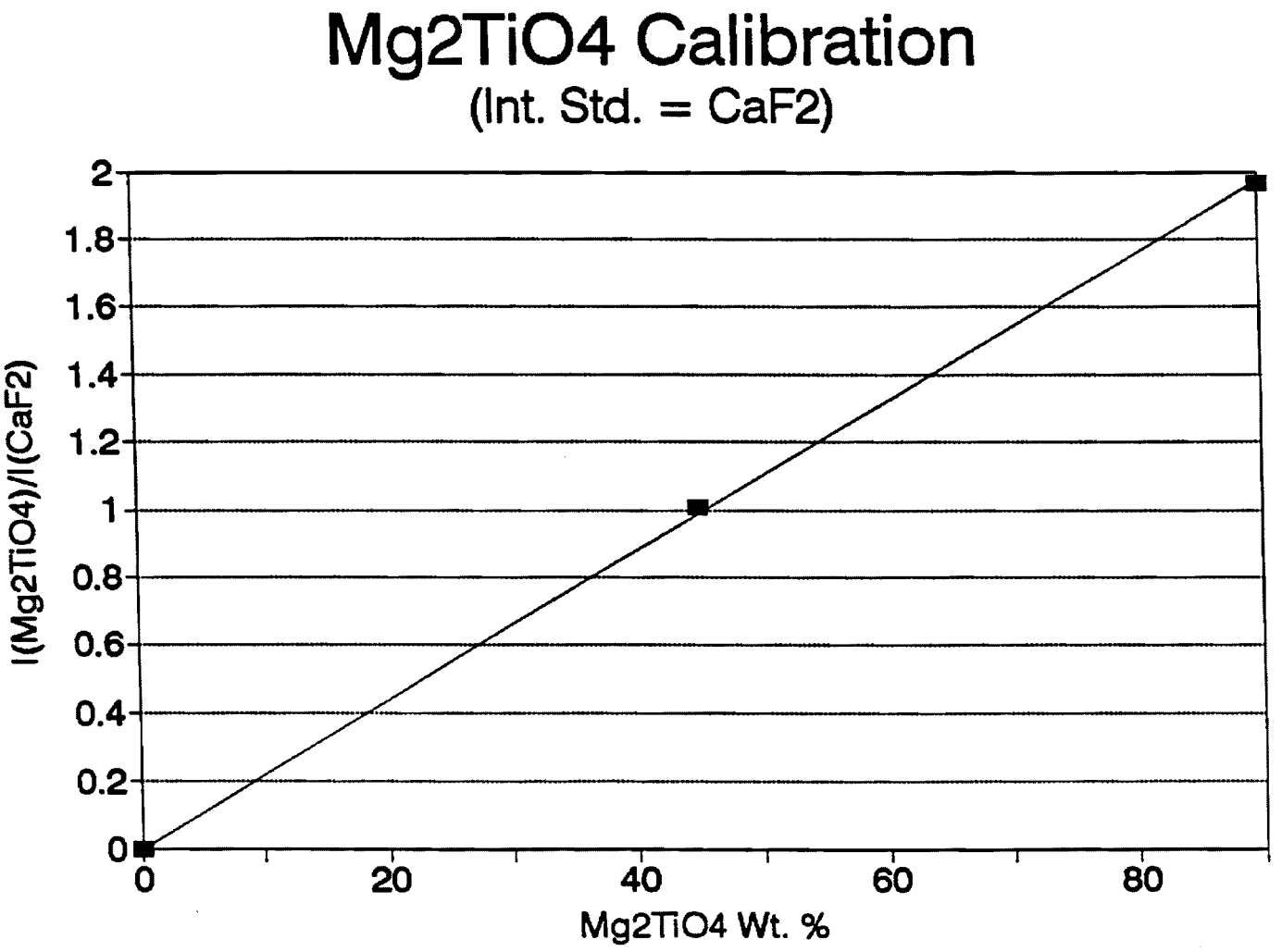
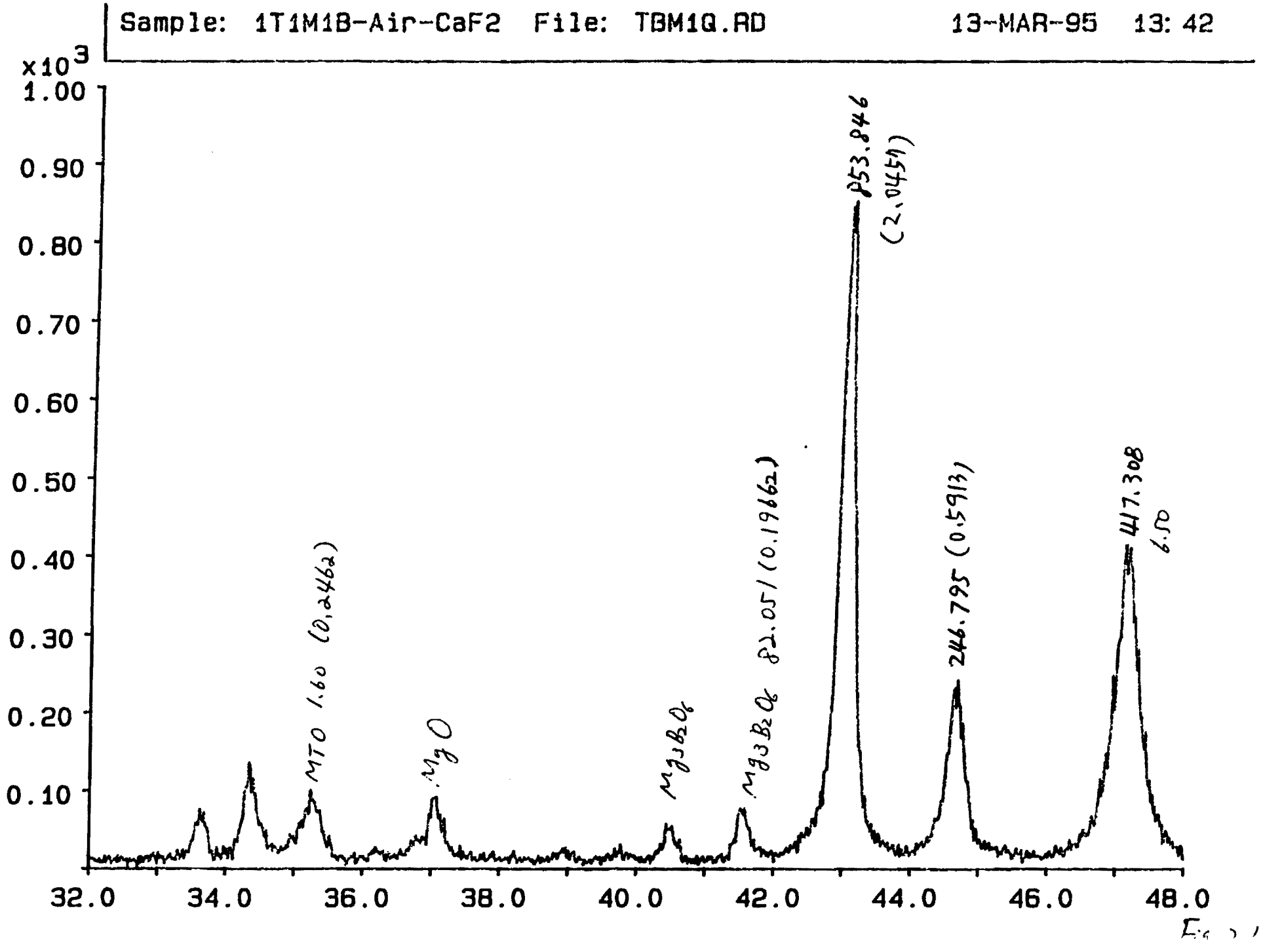
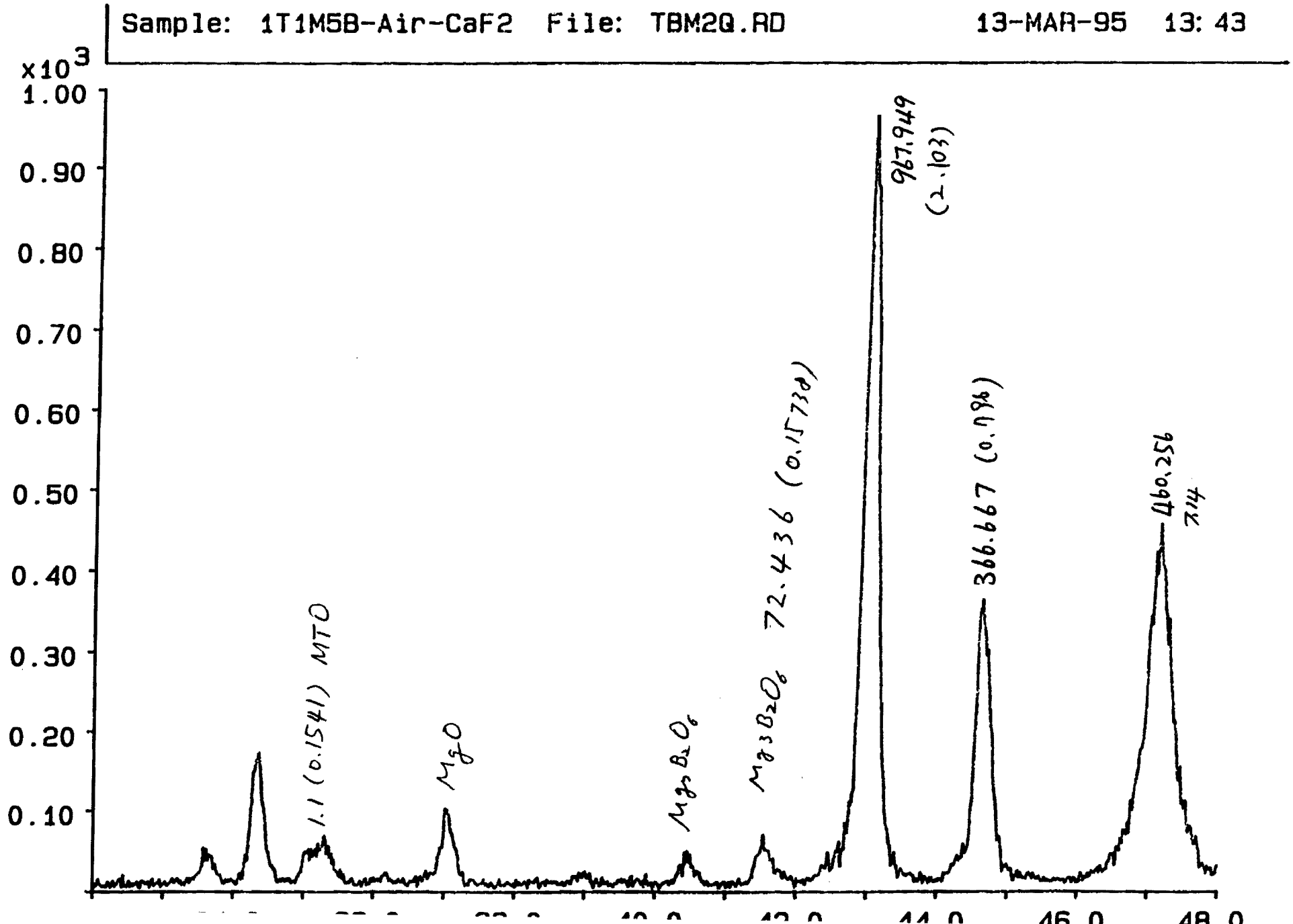

Sample: OMTO-80TiC-20CaF2 File: CAL16.RD 28-MAR-95 11:49
x10 3
2.60
2.34
2.08
1.82
1.56
1.30
1.04
0.78
0.52
0.26
14.915
(14.0708)
TiC
1.06
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0

Fig 19


Mg2TiO4 Calibration
(Int. Std. = CaF2)
I(Mg2TiO4)/I(CaF2)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
Mg2TiO4 Wt. %


Sample: 1T1M1B-Air-CaF2 File: TBM1Q.RD 13-MAR-95 13:42
x10 3
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
MTO 1.60 (0,2462)
MgO
MgB2O4
MgB2O4 42.057 (0.19862)
253.846 (2,0454)
246.795 (0.5913)
417.308
6.50


Sample: 1T1M5B-Air-CaF2 File: TBM2Q.RD 13-MAR-95 13:43
x10^3
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
1.1 (0.1541) MTO
MgO
MgBO2
Mg3B2O6
72.4436 (0.1737)
967.949
(2.103)
366.667 (0.196)
460.256
714

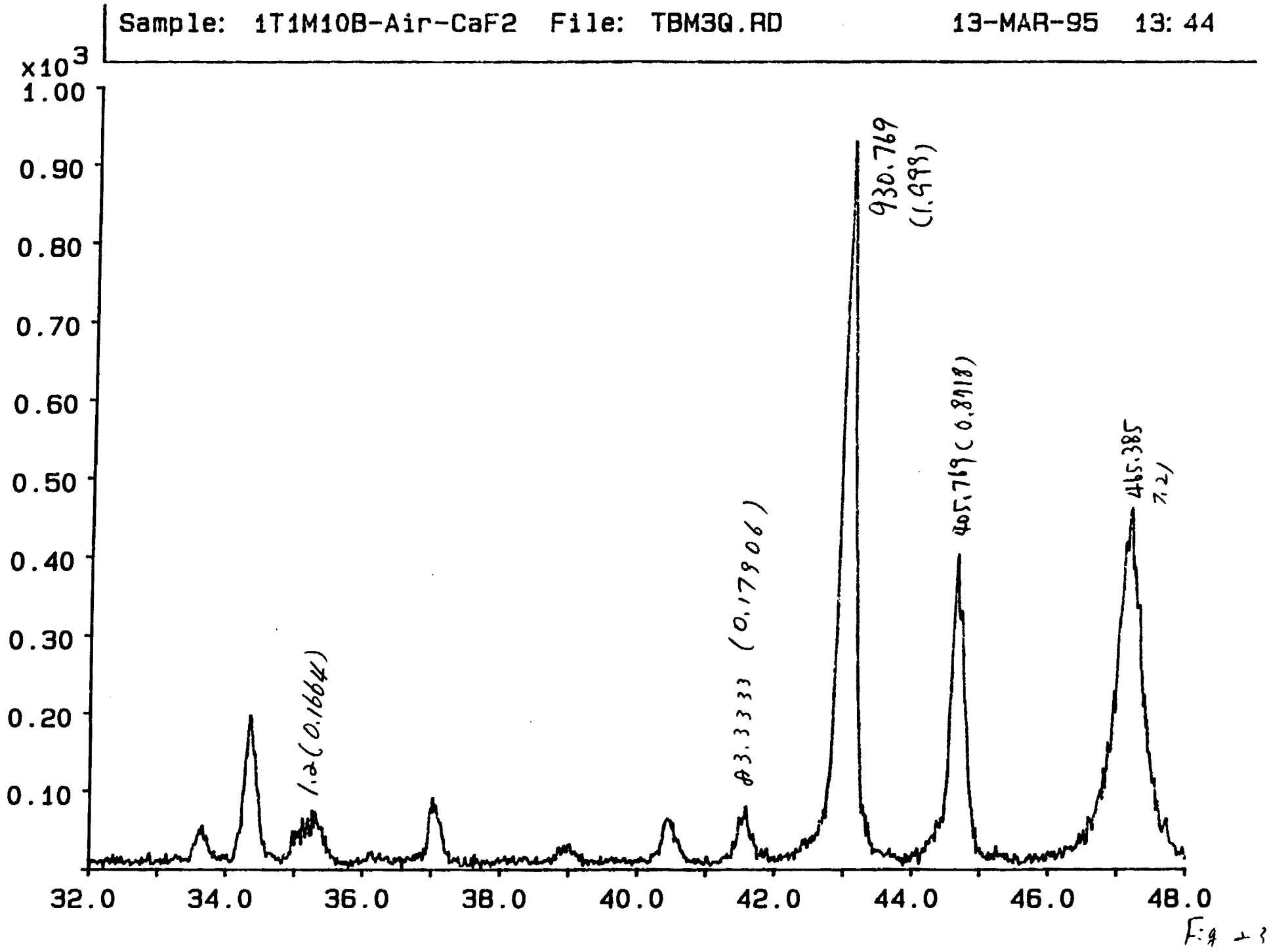
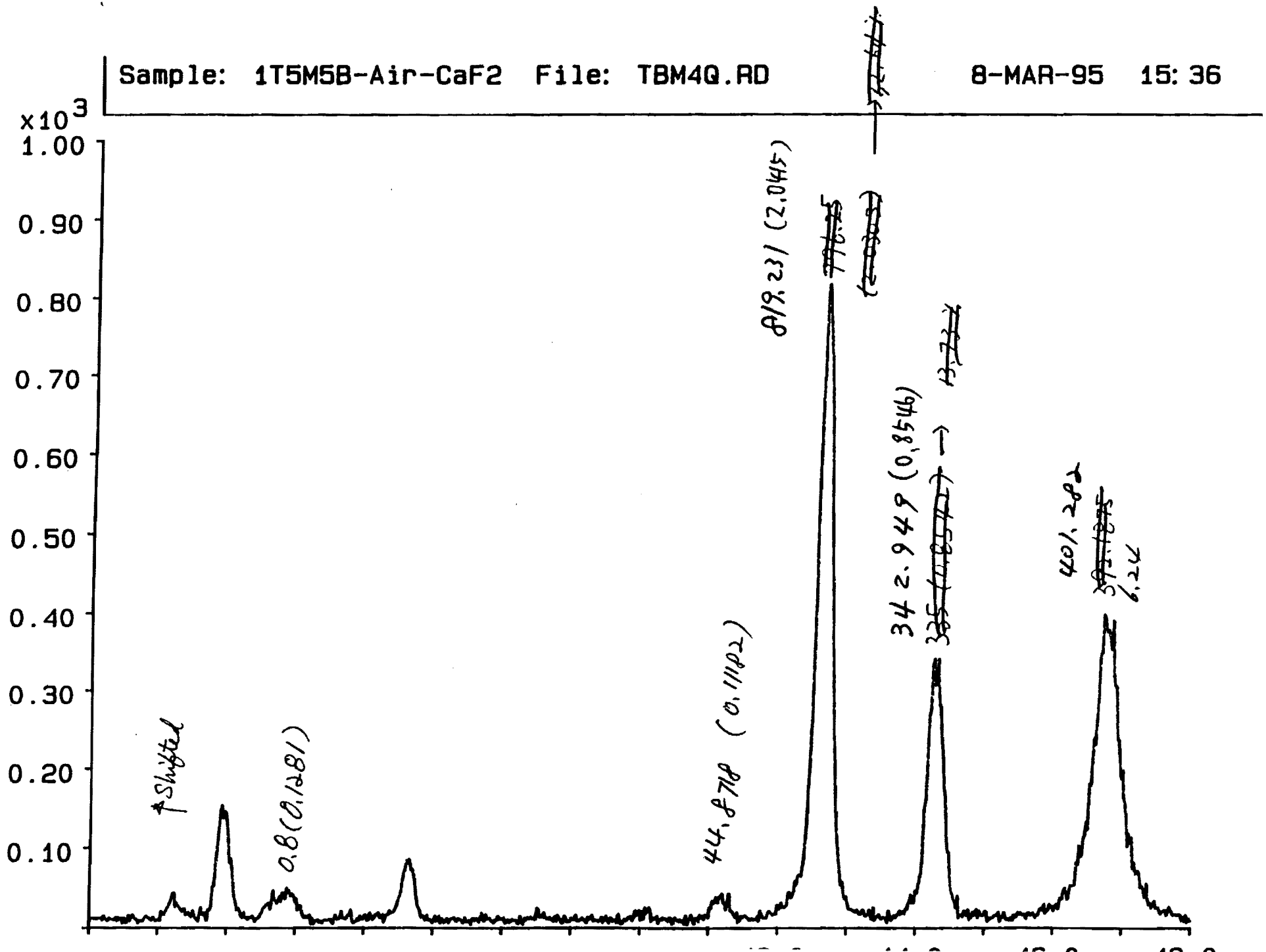
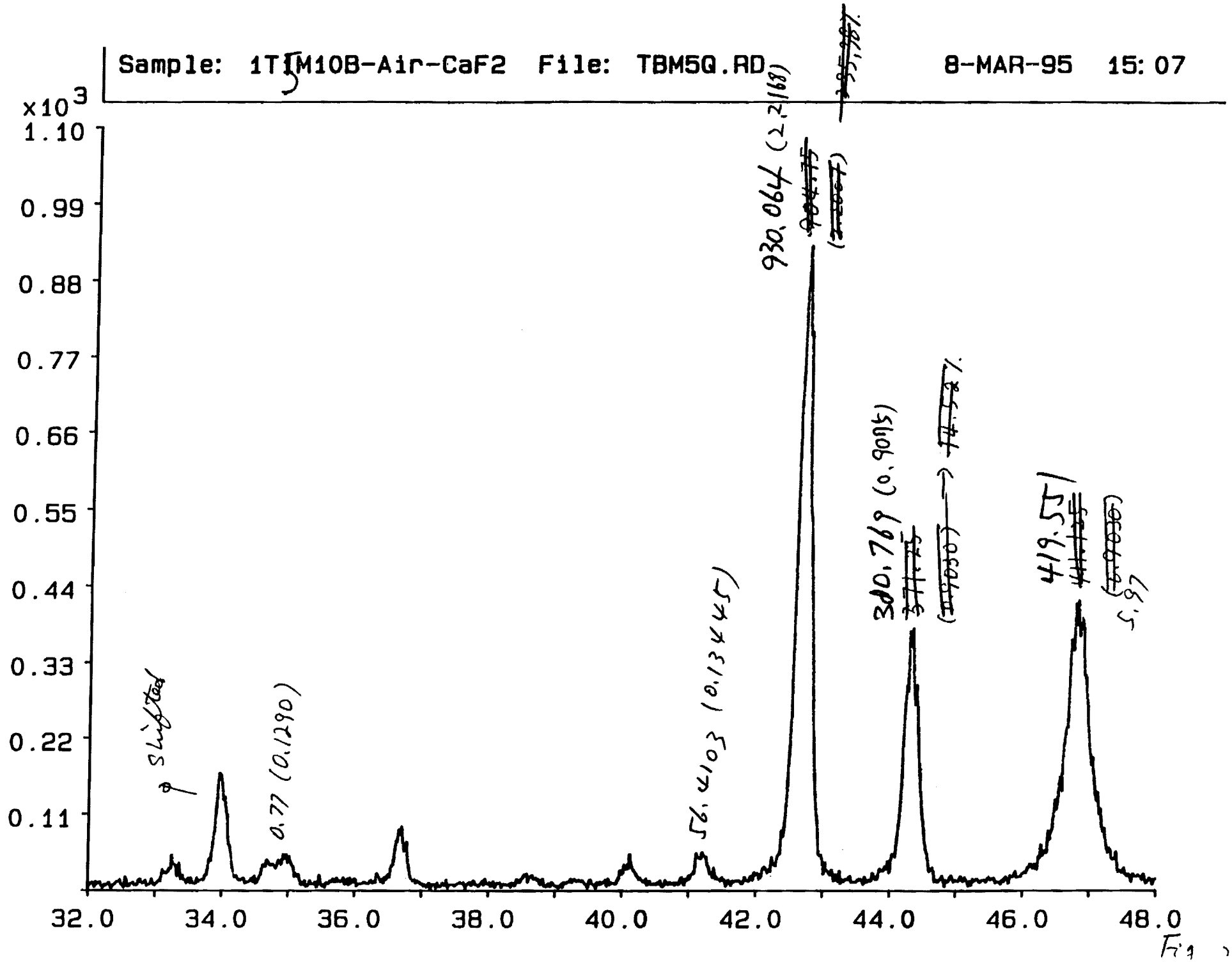
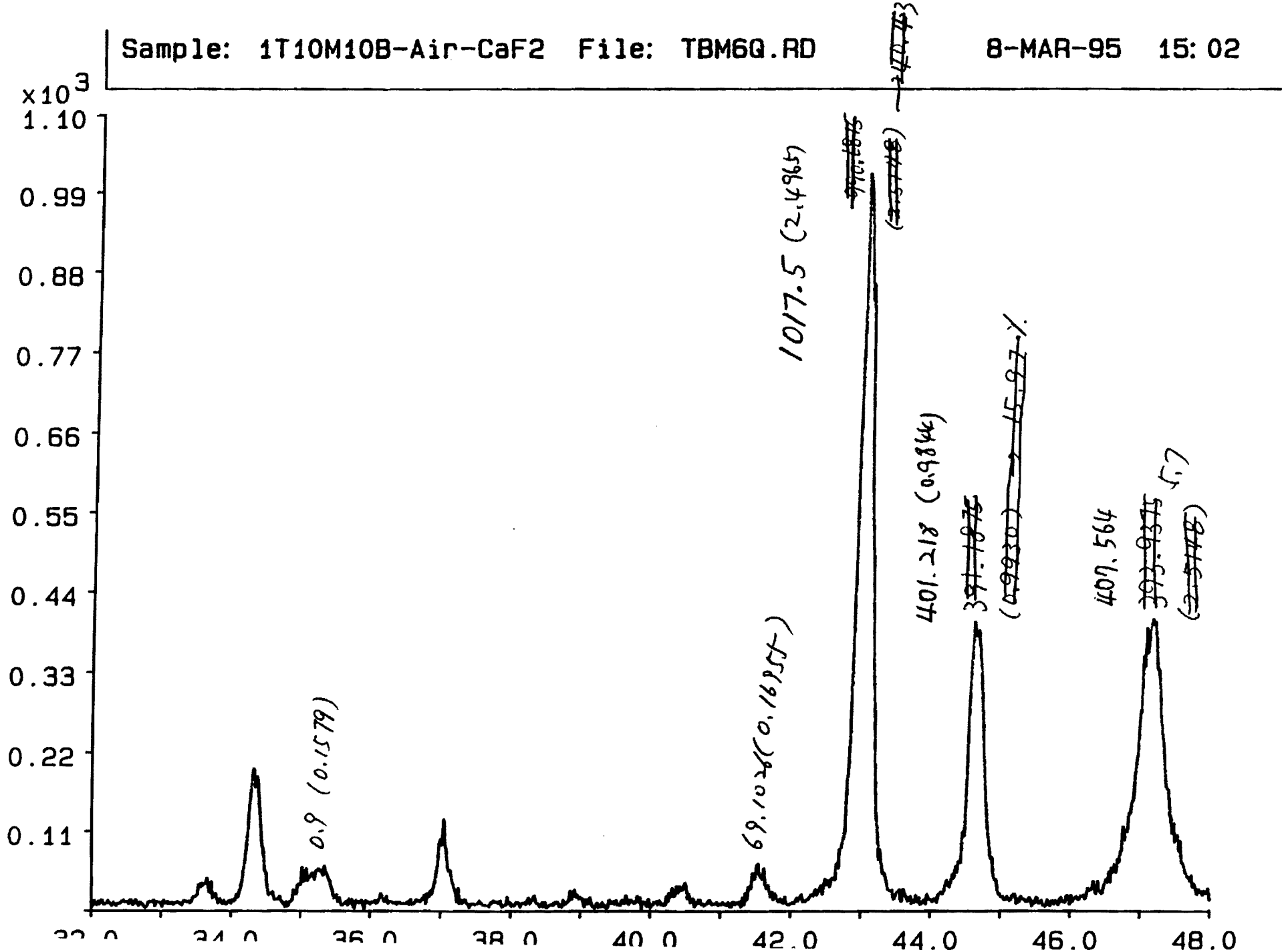

Sample: 1T1M10B-Air-CaF2 File: TBM3Q.RD 13-MAR-95 13:44
x10^3
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
930.769 (1.998)
905.769 (0.8918)
485.385 7.2)
(0.17906)

Fig 13


Sample: 1T5M5B-Air-CaF2 File: TBM4Q.RD 8-MAR-95 15: 36
x10 3
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
819.231 (2.0045)
342.9492 (0.8546)
401.208
44.8718 (0.1102)
0.8(0.1981)


Sample: 1TiM10B-Air-CaF2 File: TBM5Q.RD 8-MAR-95 15:07
x10^3
1.10
0.99
0.88
0.77
0.66
0.55
0.44
0.33
0.22
0.11
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
0.77 (0.1290)
56,4103 (0,13445)
930,064 (2,2168)
300,769 (0,9015)
419,551


Sample: 1T10M10B-Air-CaF2 File: TBM6Q.RD 8-MAR-95 15:02
x10^3
1.10
0.99
0.88
0.77
0.66
0.55
0.44
0.33
0.22
0.11
1017.5 (2.4965)
401.218 (0.9844)
401.564
0.9 (0.1579)
69.10 (0.1695)
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0

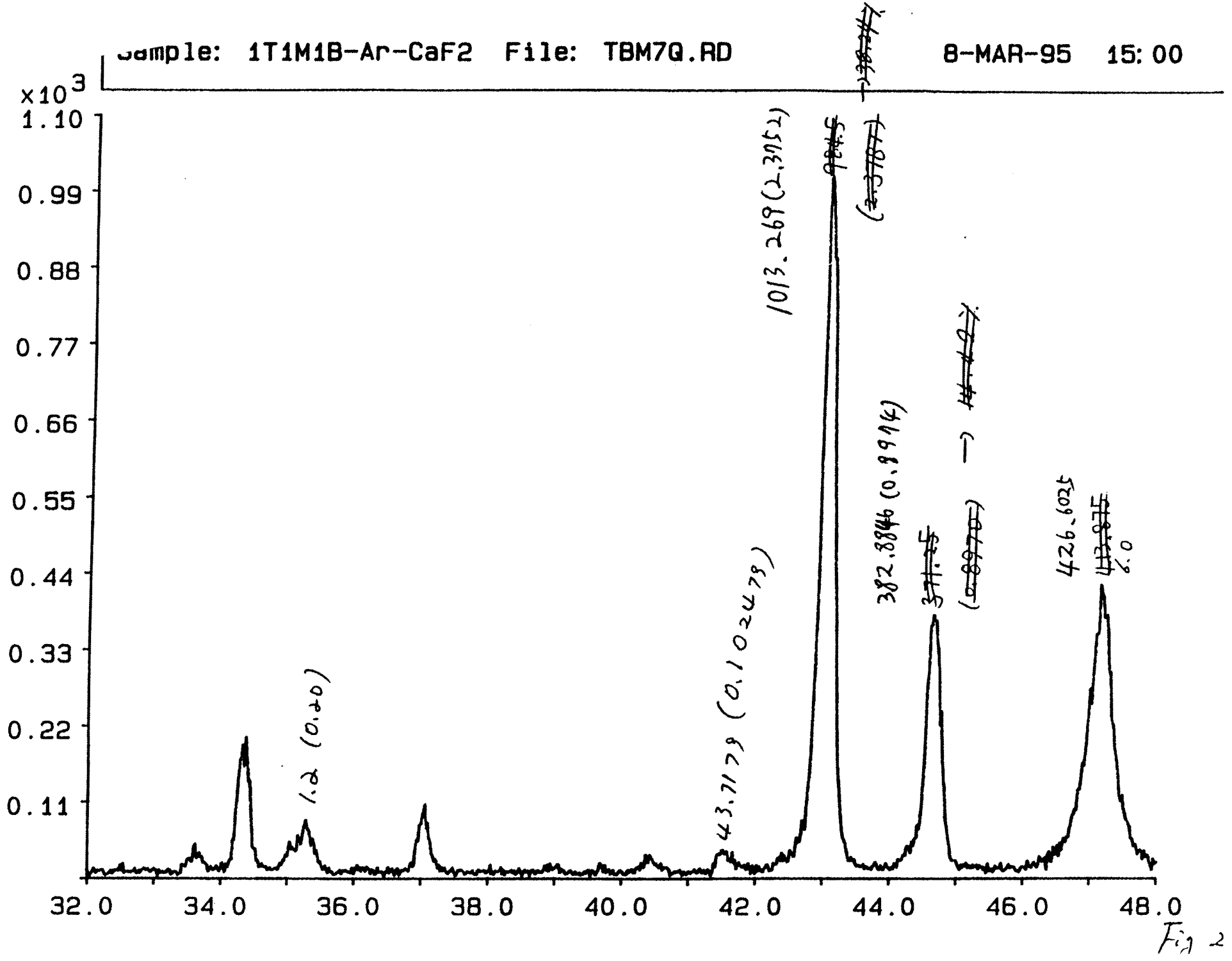
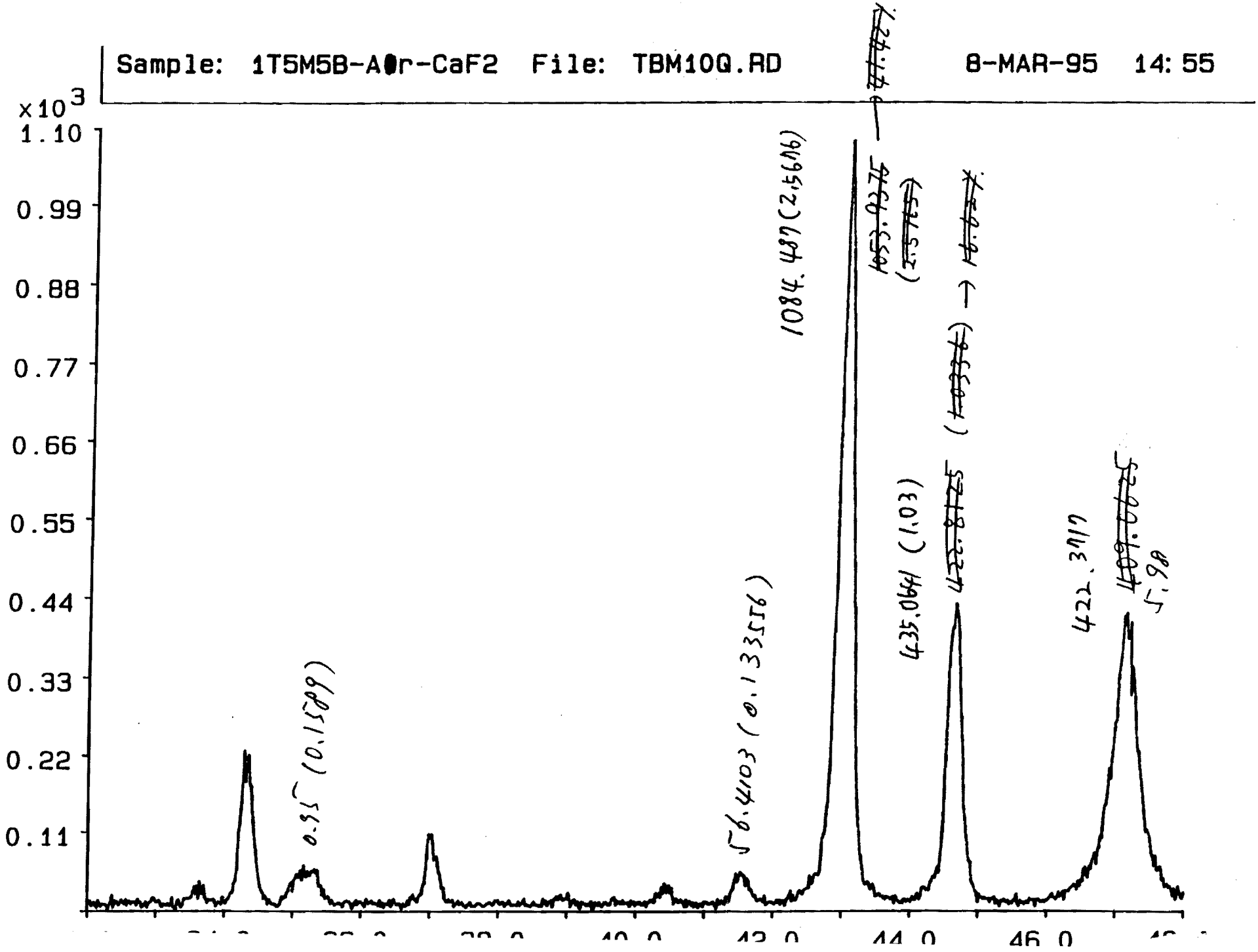

Sample: 1T1M1B-Ar-CaF2 File: TBM7Q.RD
8-MAR-95 15:00
x10 3
1.10
0.99
0.88
0.77
0.66
0.55
0.44
0.33
0.22
0.11
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
1013.269 (2.3152)
382.8846 (0.8914)
426.6025
43.7179 (0.10247)

Fig 27


Sample: 1T5M5B-A●r-CaF2 File: TBM10Q.RD 8-MAR-95 14:55
x10^3
1.10
0.99
0.88
0.77
0.66
0.55
0.44
0.33
0.22
0.11
0.35 (0.15089)
1084.487 (2.56016)
435.0644 (1.03)
422.3117
44 0
46 0

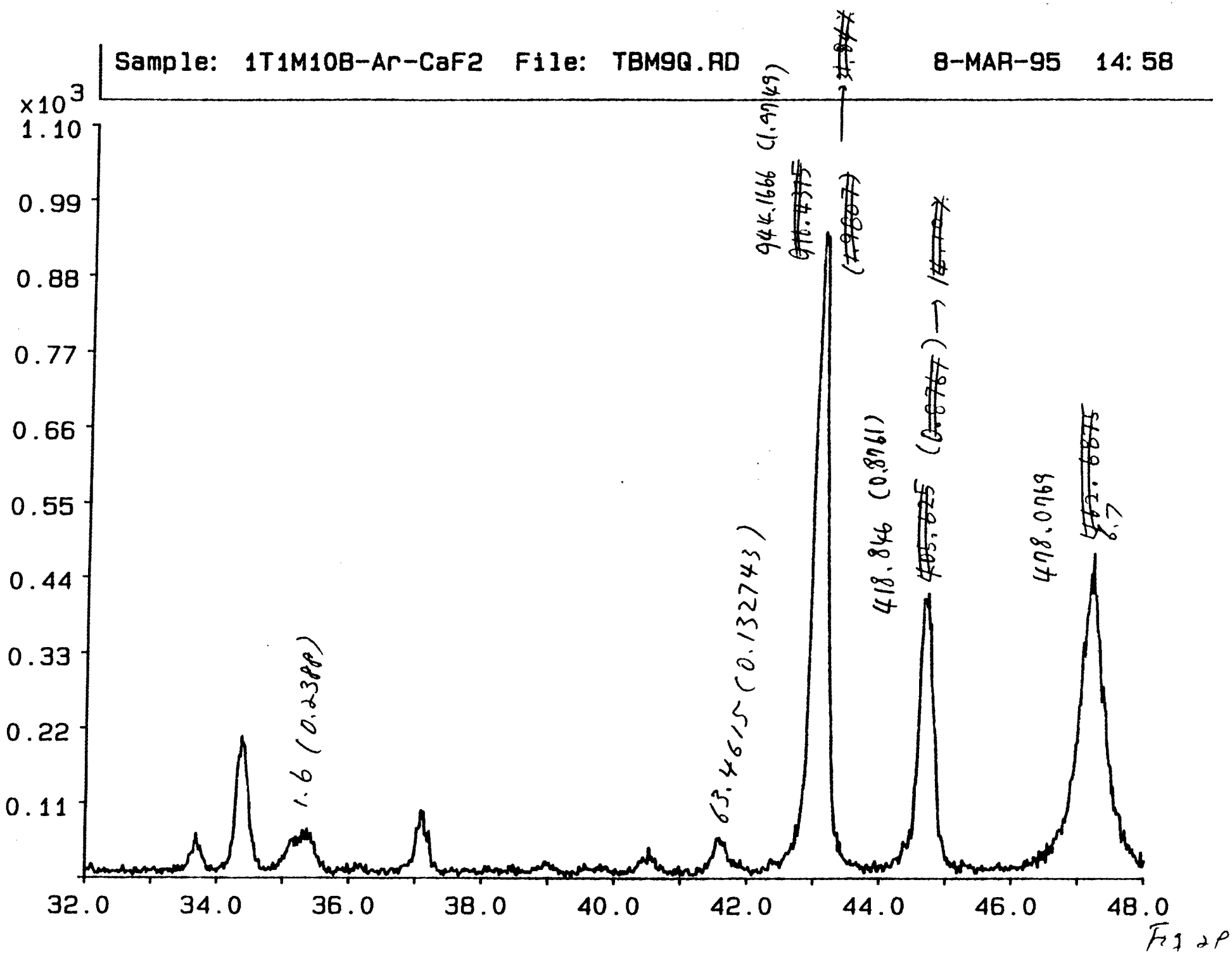
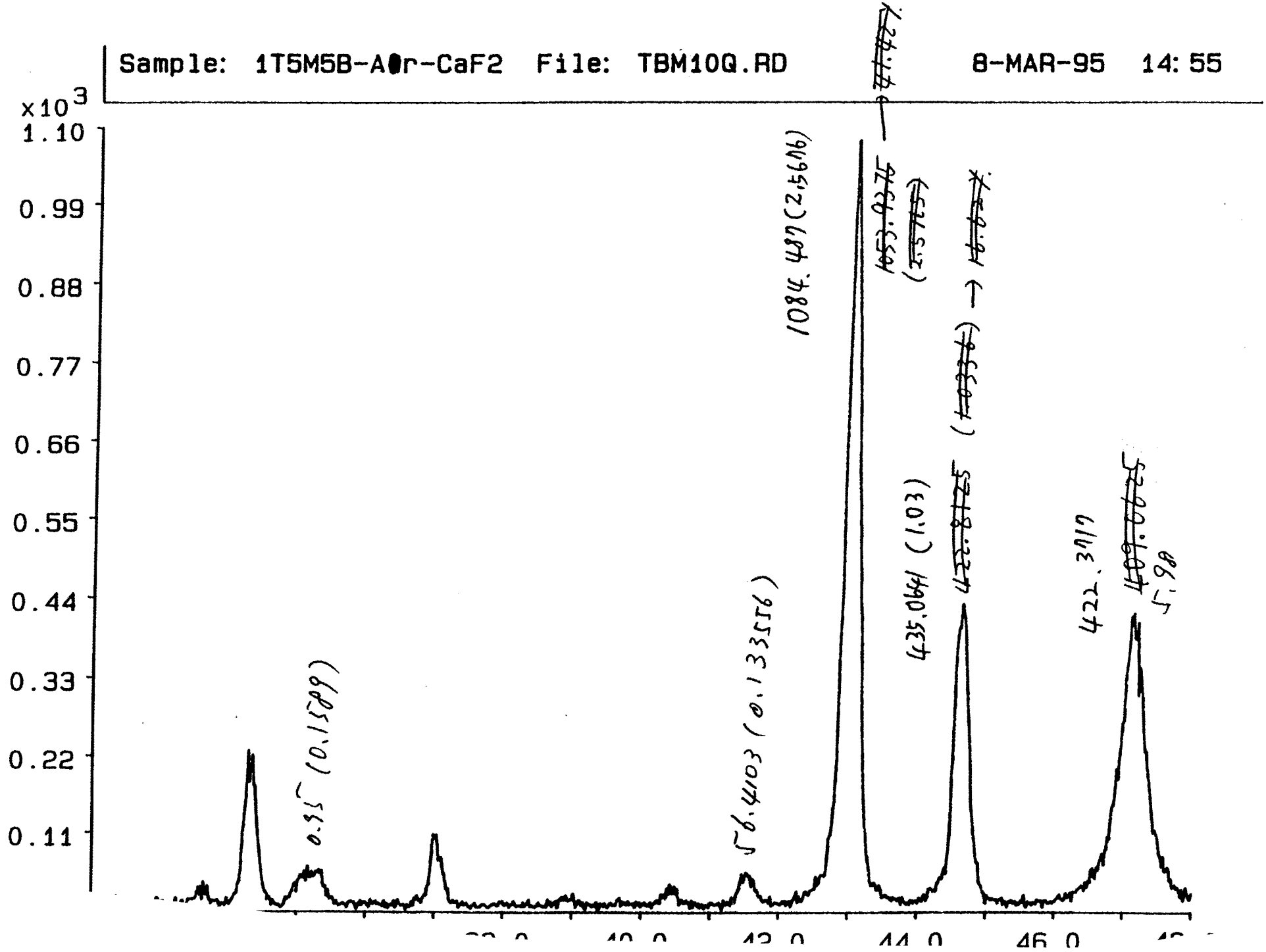

Sample: 1T1M10B-Ar-CaF2 File: TBM9Q.RD 8-MAR-95 14:58
x10^3
1.10
0.99
0.88
0.77
0.66
0.55
0.44
0.33
0.22
0.11
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
944.1666
418.846
408.0769
1.6 (0.2388)
63.4615 (0.132743)

Fig 2P


Sample: 1T5M5B-A●r-CaF2 File: TBM10Q.RD 8-MAR-95 14:55
x10^3
1.10
0.99
0.88
0.77
0.66
0.55
0.44
0.33
0.22
0.11
1084.487 (2,5616)
435.0641 (1,03)
422.3117

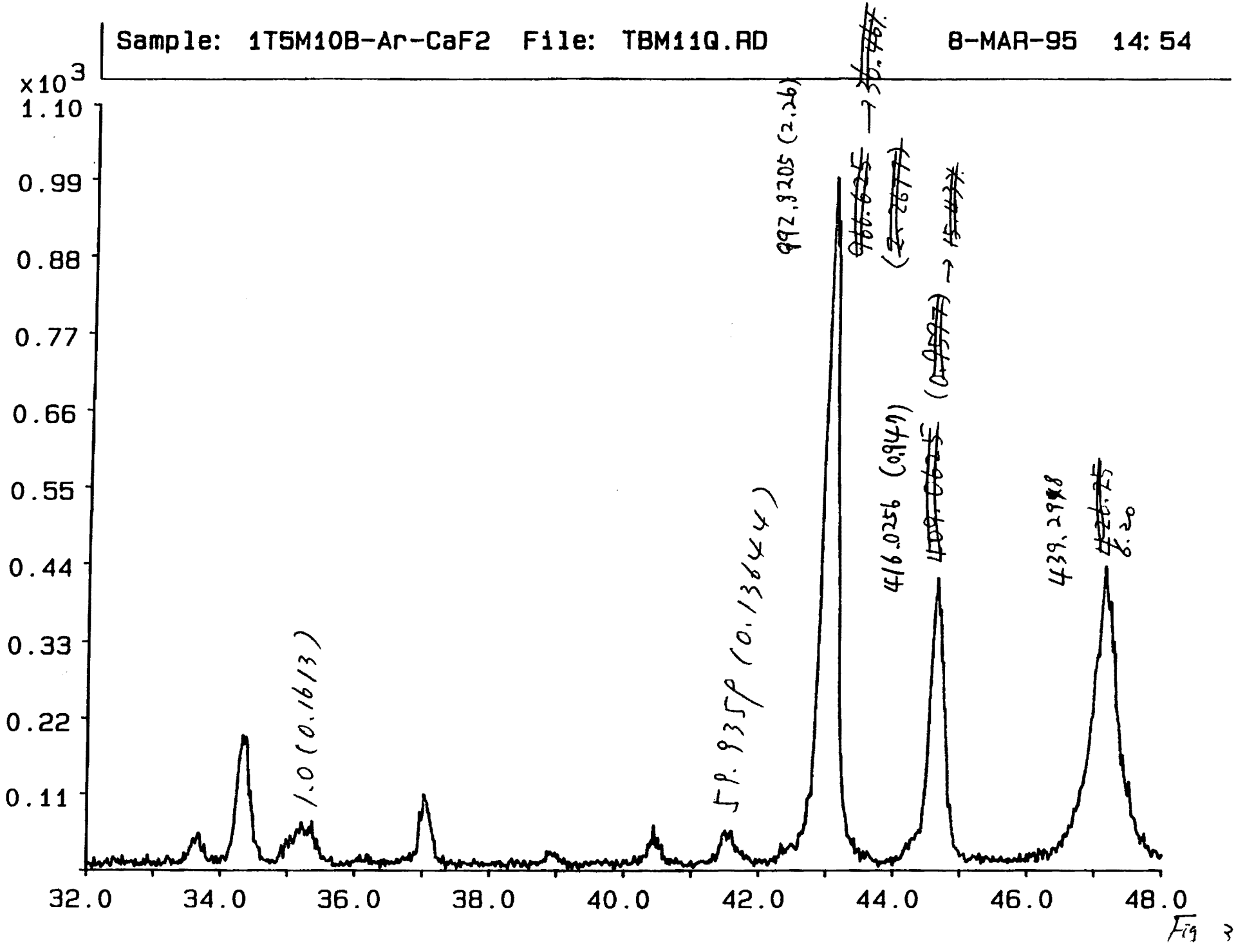
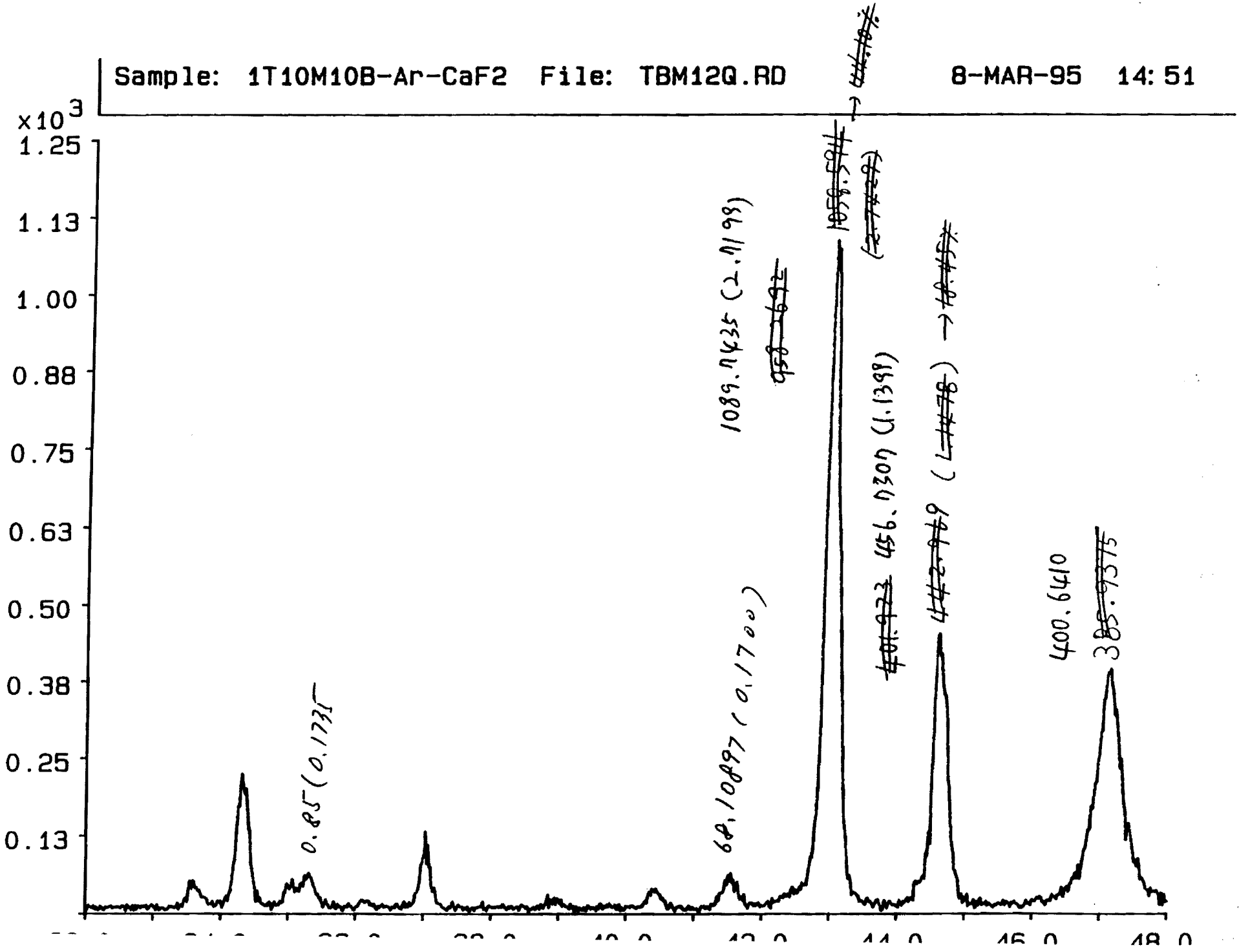

Sample: 1T5M10B-Ar-CaF2 File: TBM11Q.RD 8-MAR-95 14:54
x10 3
1.10
0.99
0.88
0.77
0.66
0.55
0.44
0.33
0.22
0.11
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
992.3205 (2.26)
416.0256 (0.94)
439.2988
1.0 (0.1613)
FP. 933P (0.13644)

Fig 31


Sample: 1T10M10B-Ar-CaF2 File: TBM12Q.RD 8-MAR-95 14:51
x10 3
1.25
1.13
1.00
0.88
0.75
0.63
0.50
0.38
0.25
0.13
0.85 (0.173)
1089.11435 (2.11 98)
1456.0309 (1.1398)
400.6410
385.9375

TO: K. V. Logan

FROM: Gautam Patel

SUBJECT: AEM Project
Progress Report (4-1-95 to 4-12-95)

DATE: April 12, 1995

1 Five SHS TiB2 reactions (S/5) have been completed and ball milled for 30 minutes. A total of 2720gm of powder was obtained after ball milling and submitted to Joel Tenney of AEM for leaching. In a few ball milled batches we found a few small to large pieces that were hard. These pieces appeared either from agglomeration of the ground powder or a few SHS reacted pieces did not ground.

2 Two hot press runs were completed.

2a: The first run was conducted using TiB2 powder (S/5). Powder was leached in a large stainless steel container. A new set of POCO XT die and punches was used. The sample was hot pressed at 6500 psi pressure and 1650 C soak temperature. Approximately 10 degree per minute heating rate was used during ramp up period. The slow heating rate was used to obtain a CTP curve. Type "C" thermocouple and a new temperature indicator were used for temperature monitoring. No argon atmosphere was used during the run. To protect the thermocouple from oxidation more carbon black was mixed with alumina bubbles and used for insulation.

After two hours and forty two minutes (ramp up time) the temperature had reached to 1650 C. The ram was continuing to show downward movement indicating densification. After two hours of soaking, the ram continued to travel at the same rate as during ramp up period. Continue soaking after two hours, the ram travel did not decrease. After three hours of soak, it started to move downward at much faster rate than the first two hours of soak. The run was discontinued.

After unloading the die set, it was found that the bottom brick support had collapsed. The SiC plates, castable high strength block, and bricks had broken into pieces. The kaowool sleeve placed between the die and silica sleeve had burnt out. It was found that more than usual amount of glassy substance had oozed out between the die and top and bottom punches. The piece was extracted from the die but was found to be less than 0.5" thick. During grinding step to remove the burrs, the disk broke into two pieces.

The density on one half of the disk was measured and found to be 97%. The fracture surface of the disk will be examined by Shin for inclusions analysis. The banded structure of the surface will also be examined to identify large particles. A CTP curve to show

the densification of the powder as a function of temperature is attached.

2b: The second hot press run was conducted using T/A composite powder. Aim was to obtain 3"d x 0.505" t disk. New POCO XT die and punches were used. Type "C" thermocouple and a new temperature indicator were used. The sample was hot pressed at 6500 psi pressure and 1620C soak temperature. It was decided to use fast heating rate during ramp up period. It was found that the cage that surrounds the coil and the die started to catch fire. The hot press has been grounded but at this high heating rate it appeared not to be properly grounded. The heating rate was reduced and arcing stopped. The run was completed within one hour and forty five minutes (one hour and eighteen minutes of ramp up time and twenty seven minutes of soak time).

The density was measured after removing the graphoil and polishing on a 165 micron diamond disk. The disk was found to be 97.4% dense and measured 0.490" thick.

A CTP curve to show the densification of the powder as a function of temperature is attached.

4 The original funded proposals A-9815, A-9833, and A-9859 were reviewed. A new proposal was written for AEM and submitted to you.

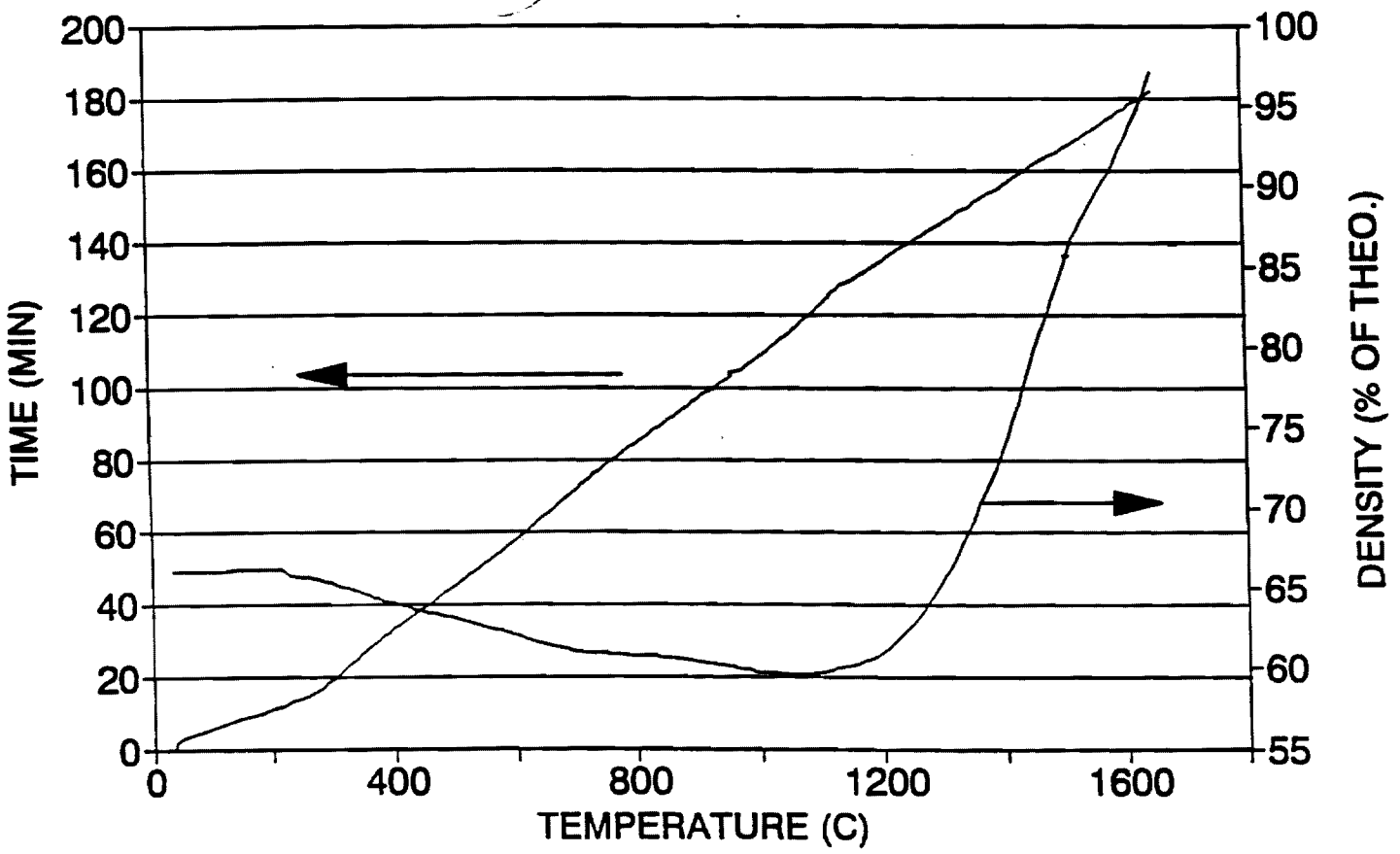
5 We do not have any castable bricks. We have four SiC plates left. We have to get new castable bricks and more SiC before the next hot press run.

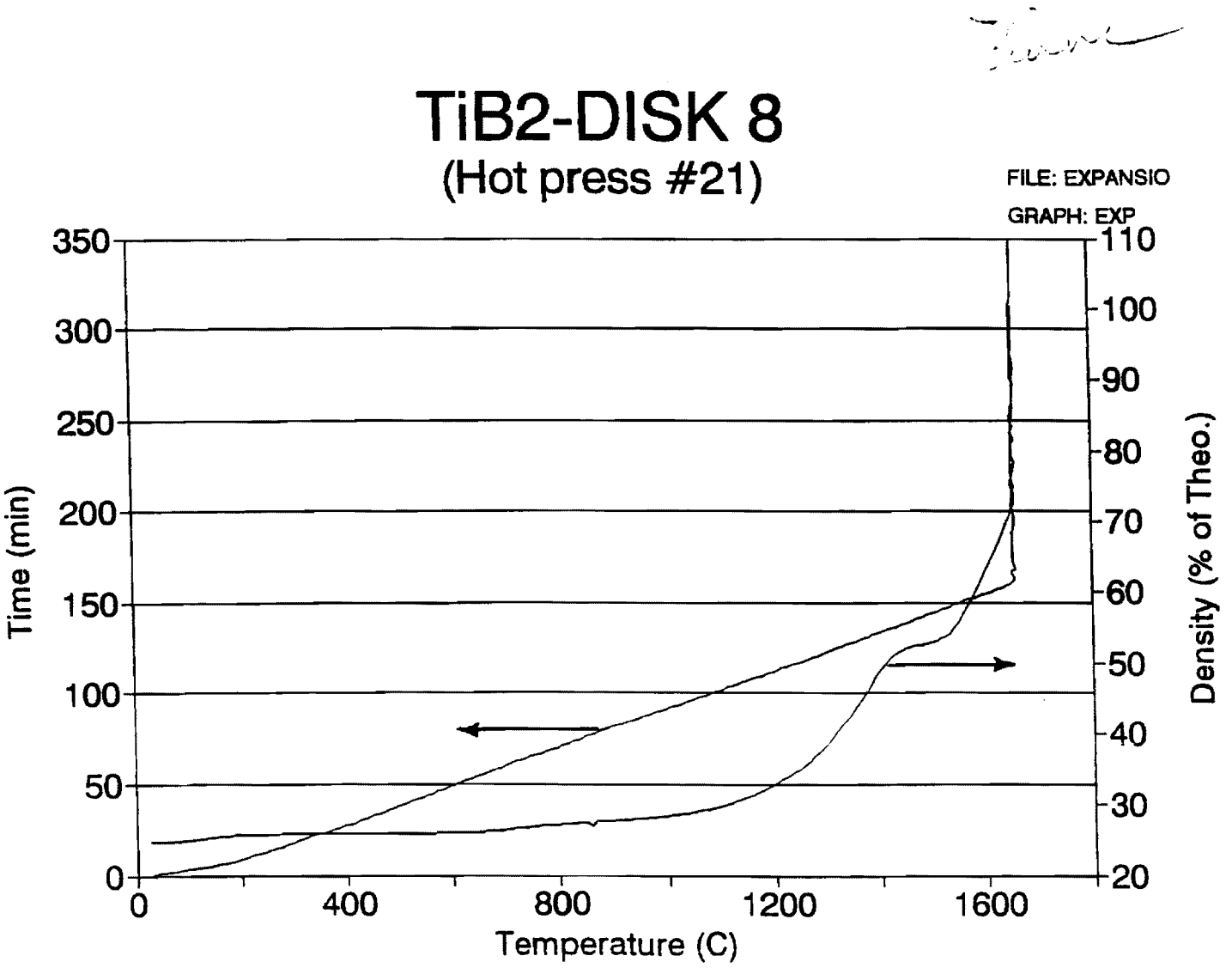
6 Shin is going to do XRD analysis on leached samples (13 samples, Paul Sykes suggested leaching method) tonight.

7 A total of thirteen T/A composite disks and eight TiB2 disks were produced. The hot pressing parameters of the T/A and TiB2 disks are shown in the attached Tables.

T/A COPMOSITE (Hot Press Run 20)

Soak temp 1650C, Soak Pressure 6500 psi




TiB2-DISK 8
(Hot press #21)
FILE: EXPANSIO
GRAPH: EXP
Time (min)
Density (% of Theo.)
Temperature (C)
350
300
250
200
150
100
50
0
110
100
90
80
70
60
50
40
30
20
0
400
800
1200
1600

TIB2 HOT PRESS

PARAMETERS

RUN	TYPE POWDER	MASS (g)	DRY-PRESS (PSI)	FINAL-PRESS (PSI)	FINAL TEMP (C)	RAMP TIME (MIN)	SOAK TIME (HOURS)	THERMOCOUPLE TYPE
1	TiB2	339.0	3374	3374	1580	28	4.16	S
2	TiB2	340.0	4499	4499]	1580	25	6:15	S
3	TiB2	340.0	4499	4499	1580	60	4.12	S
4	TiB2	340.0	4499	6501	1580	145	4:20	S
5	TiB2	340.0	4499	6501	1580	148	5:45	S
6	TiB2	340.0	5174	6074	1670/1640	98	4:00	B
7	TiB2	340.0	5062	5062	1655	34	0:14	B
8	TiB2	344.0	6501	6501	1655	162	3:00	C

TIB2 HOT PRESS

DISK DATA

DISK	DIMENSIONS DIAMETER (IN)	DIMENSIONS THICKNESS (IN)	GROSS MASS (g)	NET MASS (g)	THEORETICAL DENSITY (G/CM3)	TRUE DENSITY (G/CM3)	PERCENT DENSE
1	3.0	0.468	339.0	287.65	4.51	4.18	92.70
2	3.0		340.0	234.32	4.51	4.33	95.96
3	3.0	0.534	340.0	248.02	4.51	4.13	91.60
4	3.0	0.484	340.0	236.80	4.51	4.16	92.30
5	3.0	0.504	340.0	227.80	4.51	4.23	93.7
6	3.0	0.476	340.0	241.85	4.51	4.35	96.40
7	3.0	0.409	295.5	154.59	4.51	4.15	91.91
8	3.0	0.405	344.0	212.30	4.51	4.38	97.00

T/A HOT PRESS

PARAMETERS

RUN	TYPE POWDER	MASS (g)	DRY-PRESS (PSI)	FINAL-PRESS (PSI)	FINAL TEMP (C)	RAMP TIME (MIN)	SOAK TIME (HOURS)	THERMOCOUPLE TYPE
1	T/A COMP	240.0	3374	5399	1500		1:51	B
2	T/A COMP	239.7	3374	6298	1500	20	2:55	S
3	T/A COMP	239.8	3374	6501	1525	25	1:54	S
4	T/A COMP	239.9	3374	6501	1580	35	1:35	S
5	T/A COMP	239.8	3374	6501	1580	24	NA	S
6	T/A COMP	239.8	3374	6501	1580	20	2:10	S
7	T/A COMP	239.8	3374	6501	1580	25	2:50	S
8	T/A COMP	239.8	5624	5624	1580	22	3:08	S
9	T/A COMP	240.0	4499	6501	1580	25	1:00	S
10	T/A COMP	239.0	4499	6501	1580	60	0:55	S
11	T/A COMP	239.0	1125	6501	1580	65	2:35	S
12	T/A COMP	188.86	6501	6501	1650	182	0:11	C
13	T/A COMP	244.50	6501	6501	1620	58	0:22	C

T/A HOT PRESS

DISK DATA

DISK	DIMENSIONS DIAMETER (IN)	DIMENSIONS THICKNESS (IN)	GROSS MASS (g)	NET MASS (g)	THEORETICAL DENSITY (G/CM3)	TRUE DENSITY (G/CM3)	PERCENT DENSE
1	3	0.545	240.0	238.50	4.14	3.79	91.55
2	3.0465	0.55	239.7	238.13	4.14	3.72	89.86
3	3.039	0.512	239.8	233.79	4.14	3.93	94.93
4	3.041	0.495	239.9	233.50	4.14	4.04	97.58
5	3.048	0.612	239.8		4.14		
6	3.053	0.543	239.8	236.51	4.14	3.80	91.79
7	3.041	0.473	239.8	222.46	4.14	3.96	95.65
8	3.000		239.8	224.70	4.14	3.93	94.5
9	3.000	0.508	240.0	178.38	4.14	4.02	97.15
10	3.000	0.496	239.0	178.55	4.14	4.04	97.60
11	3.000	0.500	239.0	178.00	4.14	4.03	97.30
12	2.65	0.366	188.86	174.88	4.14	4.00	96.60
13	3.00	0.490	244.50	234.30	4.14	4.04	97.40

NOTES:
Run 1 to 5 - POCO PGCS-3 Dies
Run 6 to 11 - POCO XT Dies
Run 1 to 7 - 8 hr. ball mill powder
Run 8 to 11 - 30 hr. ball mill powder

file:apr17.aem

Efforts to Minimize $Mg_3B_2O_6$ Phase in the Reaction Products in the SHS of TiB_2

April 24, 1995

Hyunho Shin

School of Materials Science and Engineering,

Georgia Institute of Technology, Atlanta, GA 30332.

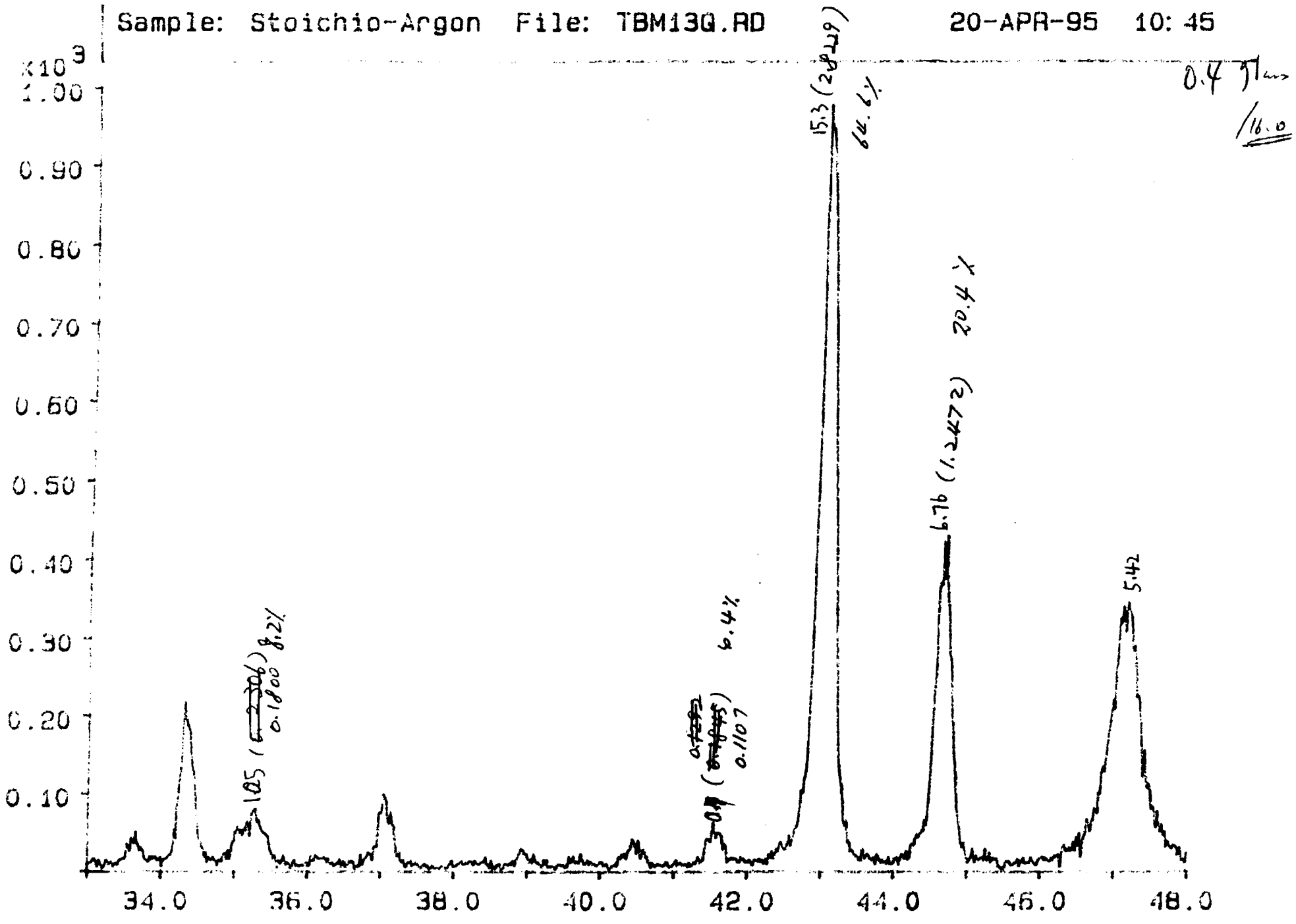
I Introduction

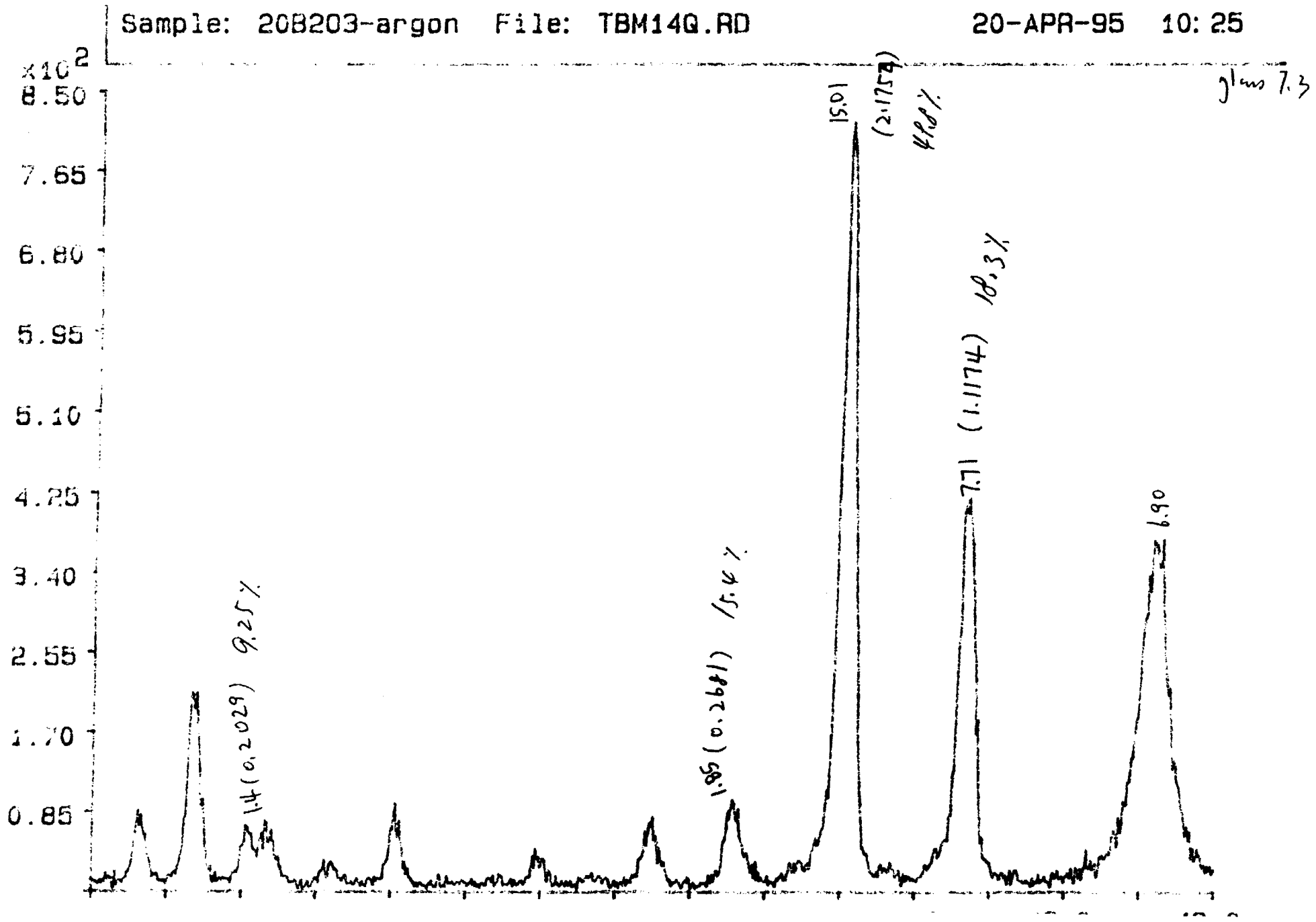
As previously reported (Jan. 20, 1995), borate is the most hard phase to eliminate by the chemical leaching we are using. Several efforts endeavored during the week of April 17, 1995 include: (1) investigating wide range of batch composition, (2) increasing the reaction temperature by igniting the reaction in a vacuum furnace, (3) decreasing the reaction temperature by the addition of TiB_2 diluent, (4) investigation of Mg-Ti-B_2O_3 system, (5) direct reaction of Ti and B. Chemical leaching was also additionally aimed using 5 and 7.5 vol% HCl acid solution.

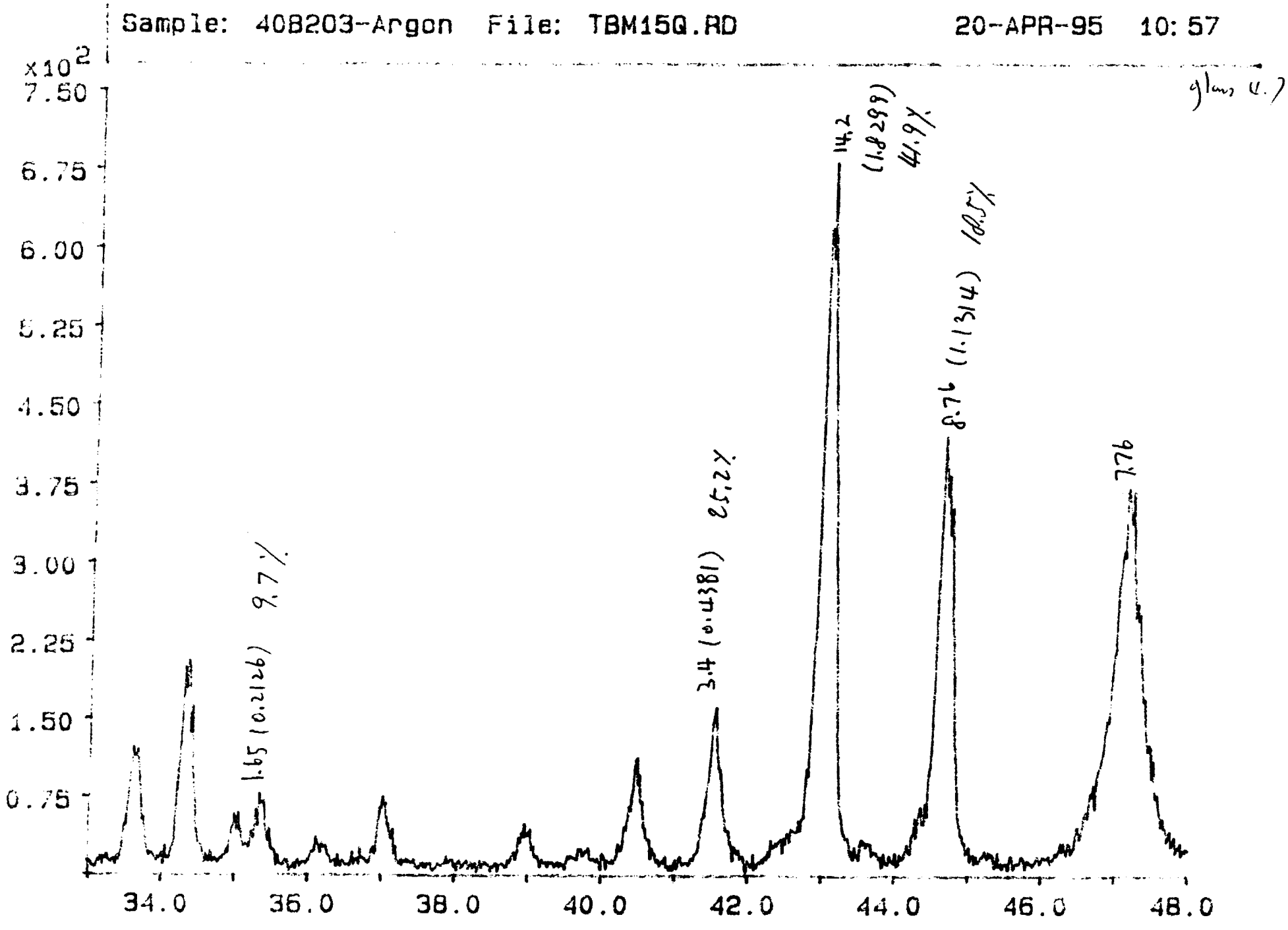
II Effect of Batch Composition

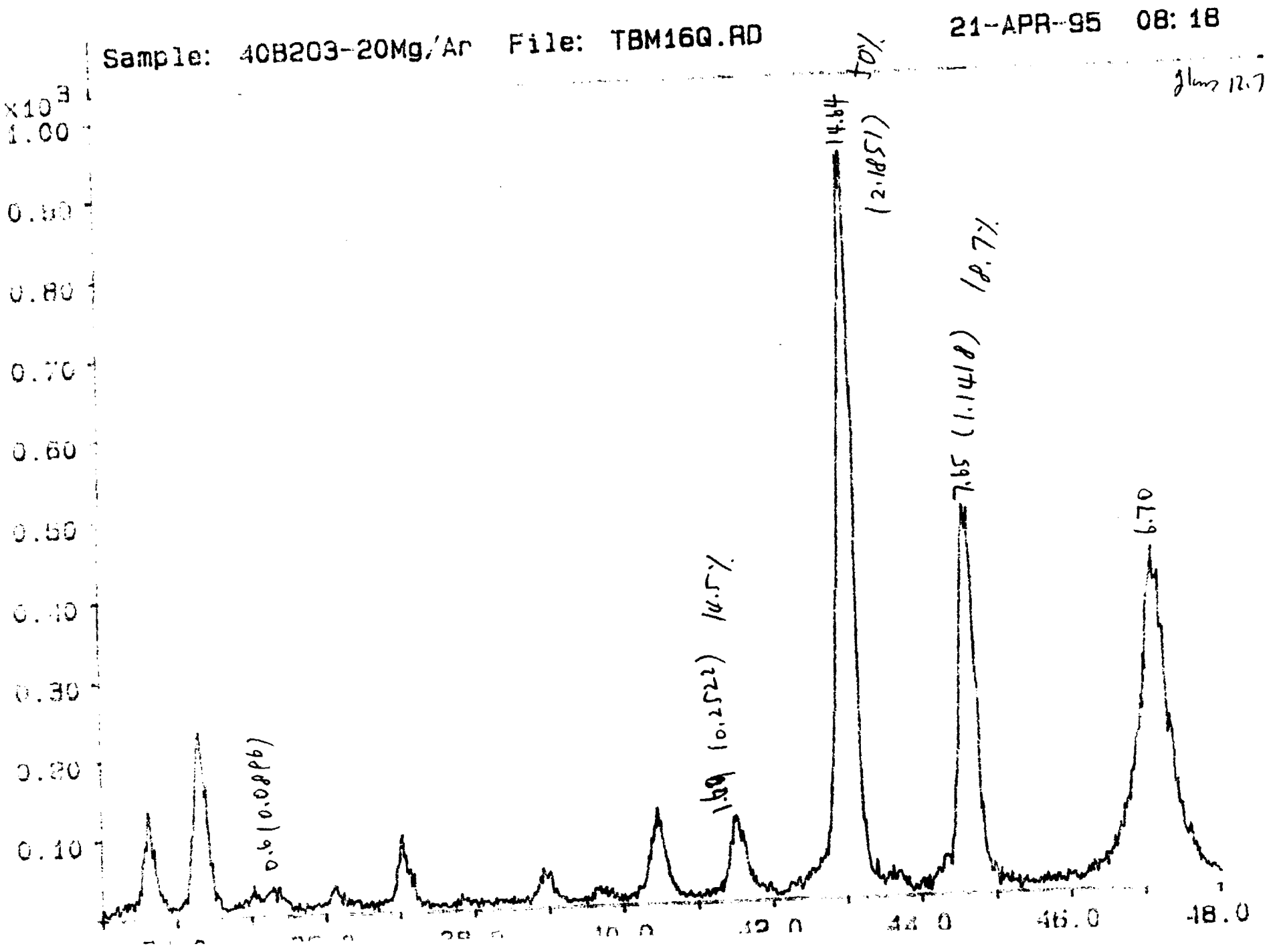
Sample	TiB_2	MgO	$Mg_3B_2O_6$	Mg_2TiO_4	glass
1T1M1B-O	9.7	46.8	11.3	11.2	21.0
1T1M5B-O	13.0	48.1	9.1	7.0	22.8
1T1M10B-O	14.3	45.7	10.3	7.6	22.1
1T5M5B-O	14.0	46.7	6.4	5.8	27.1
1T5M10B-O	14.8	50.7	7.7	5.9	20.9
1T10M10B-O	16.1	57.1	9.8	7.2	9.8
1T1M1B-Ar	14.7/20.4	54.3/64.6	5.9/6.4	9.1/8.2	16.0/0.4
1T1M5B-Ar	15.4	53.7	9.1	7.1	14.7
1T1M10B-Ar	14.3	45.2	7.6	10.9	22.0
1T5M5B-Ar	16.8	58.7	7.7	7.2	9.6
1T5M10B-Ar	15.5	51.7	7.9	7.4	17.5
1T10M10B-Ar	18.6	62.2	9.8	7.9	1.5
1T1M20B-Ar	18.3	49.8	15.4	9.3	7.3
1T1M40B-Ar	18.5	41.9	25.2	9.7	4.7
1T20M40B-Ar	18.7	50.0	14.5	5.0	12.7
1T20M1B-Ar	19.7	70.0	4.7	3.1	0.4
Nishiyama-O	15.3	15.7	19.8	2.4	46.7

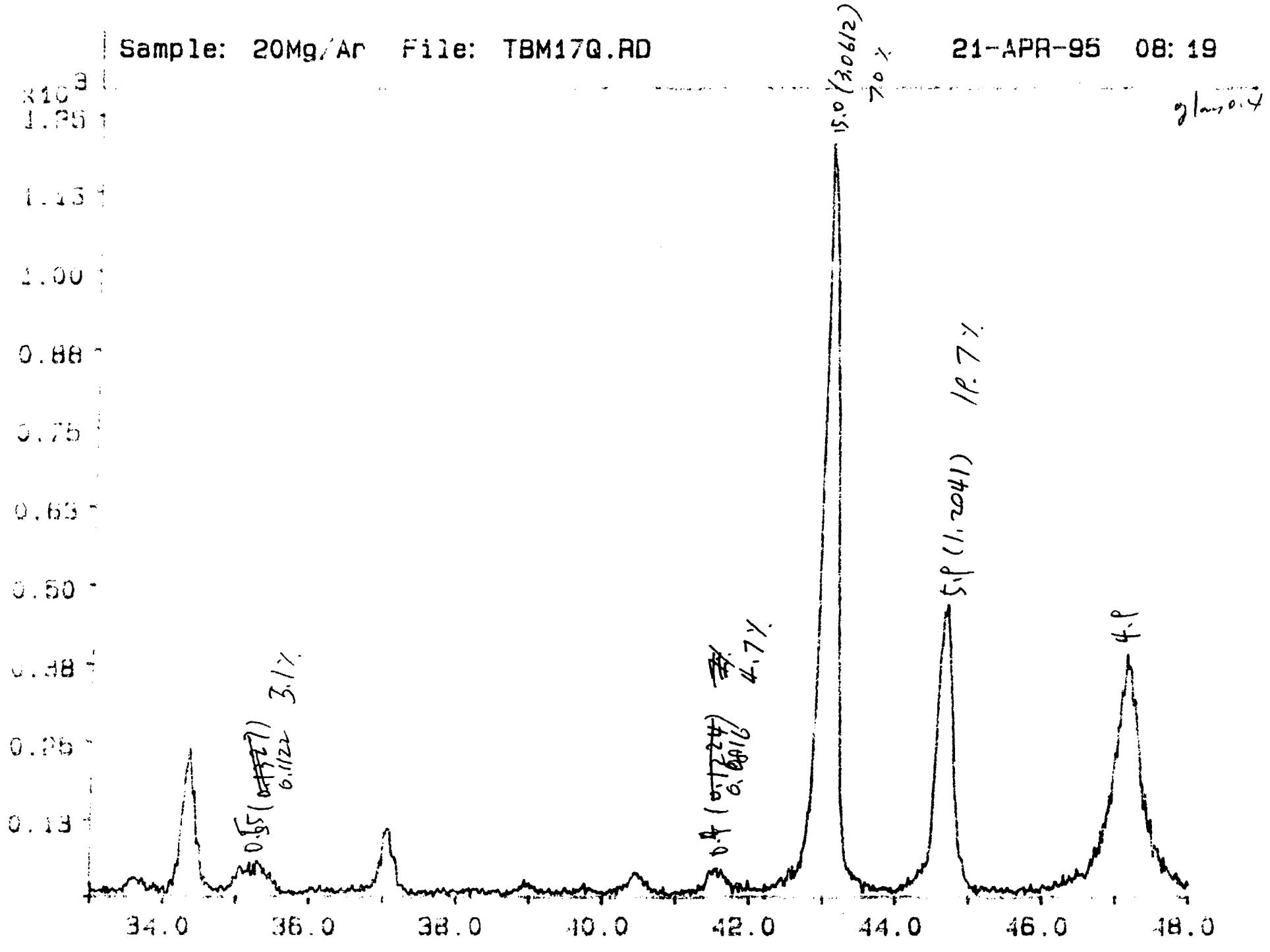
Table 1: Effect of batch composition on the reaction products. First run/Second run. Numbers represent their weight percentages.

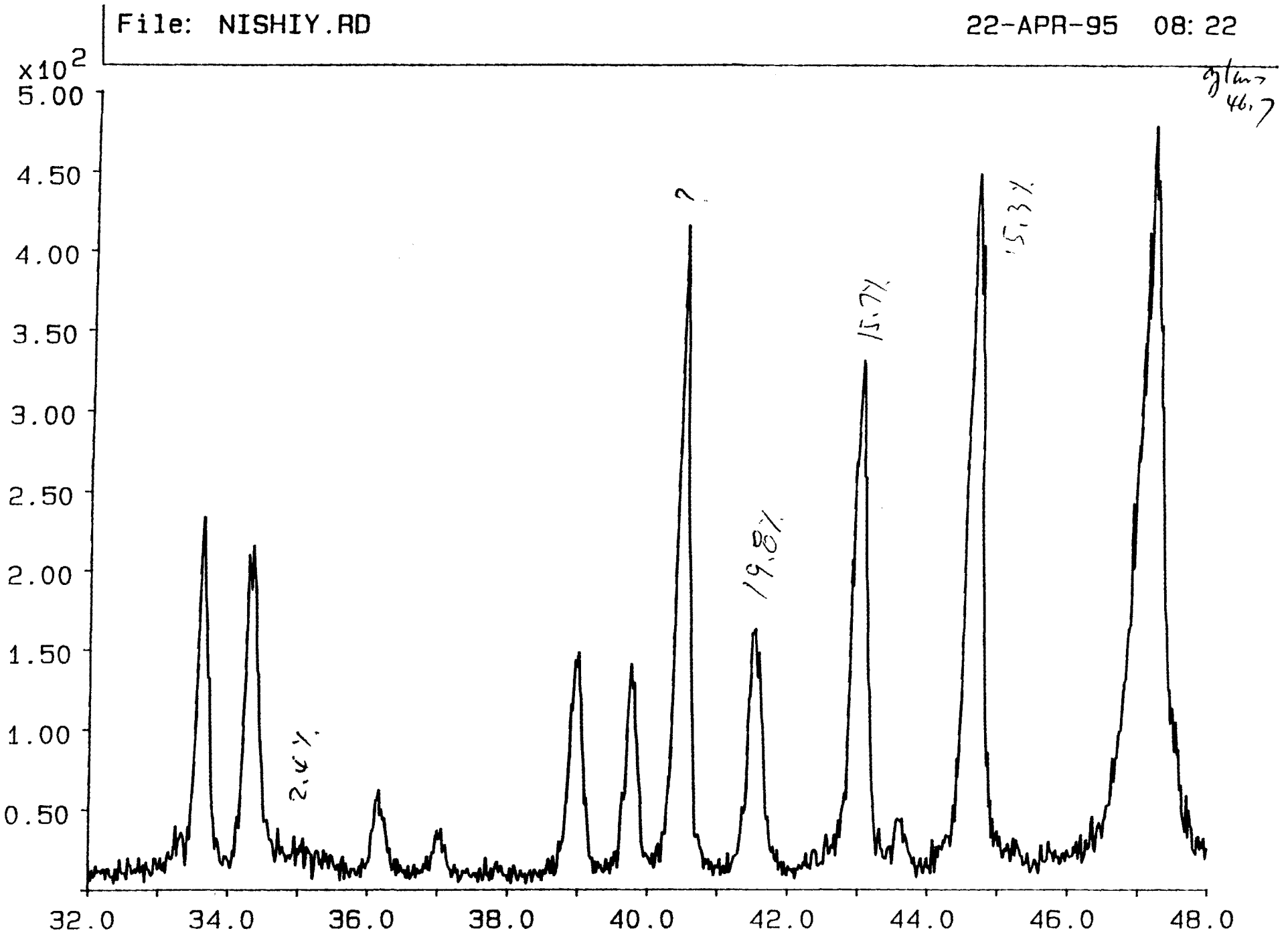

Sample: Stoichio-Argon File: TBM13Q.RD 20-APR-95 10:45
X10 3
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
15.3 (2.8439)
6.76 (1.2472)
5.42


Sample: 20B203-argon File: TBM14Q.RD 20-APR-95 10:25
x10 2
8.50
7.65
6.80
5.95
5.10
4.25
3.40
2.55
1.70
0.85
1.4 (0.2029) 9.2%
1.85 (0.2681) 15.4%
15.01
(2.1757)
41.8%
7.71 (1.1174) 18.3%
6.90


Sample: 408203-Argon File: TBM15Q.RD 20-APR-95 10:57
x10 2
7.50
6.75
6.00
5.25
4.50
3.75
3.00
2.25
1.50
0.75
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
1.65 (0.2126) 9.7%
3.4 (0.4381) 25.2%
14.2 (1.8299) 44.9%
8.76 (1.1314) 18.5%
7.76
glass ?


Sample: 40B203-20Mg/Ar File: TBM16Q.RD
21-APR-95 08:18
x10 3
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.9 (0.0886)
1.69 (0.2272) 14.5%
14.44 (2.1851) 70%
7.65 (1.1418) 10.7%
6.70
46.0
48.0

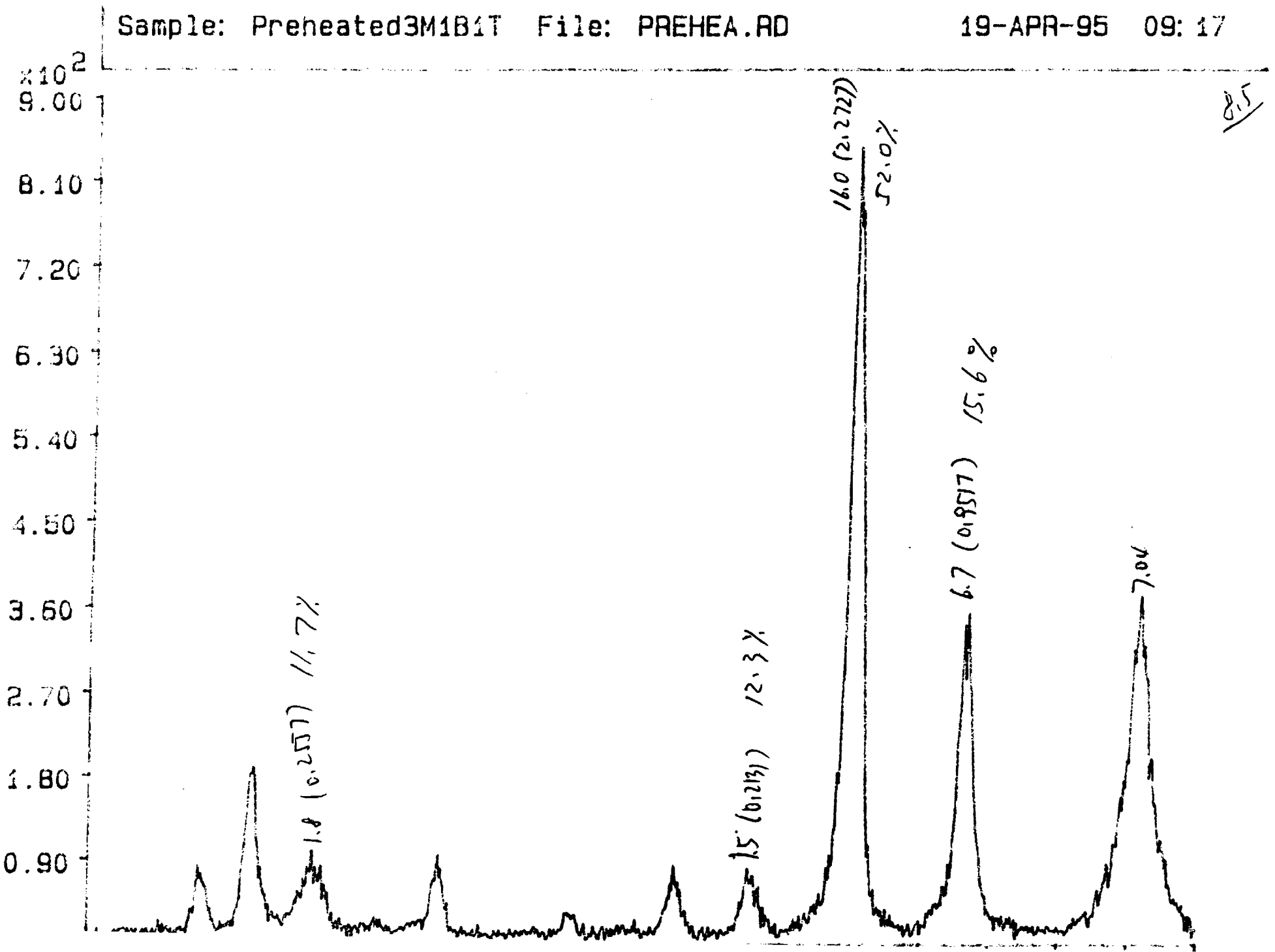

Sample: 20Mg/Ar File: TBM17Q.RD
21-APR-95 08:19
X10 3
1.25
1.13
1.00
0.88
0.75
0.63
0.50
0.38
0.25
0.13
15.0 (30612)
70 %
3.1%
4.7%
5.P (1,2041)
18.7 %
4.P
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0

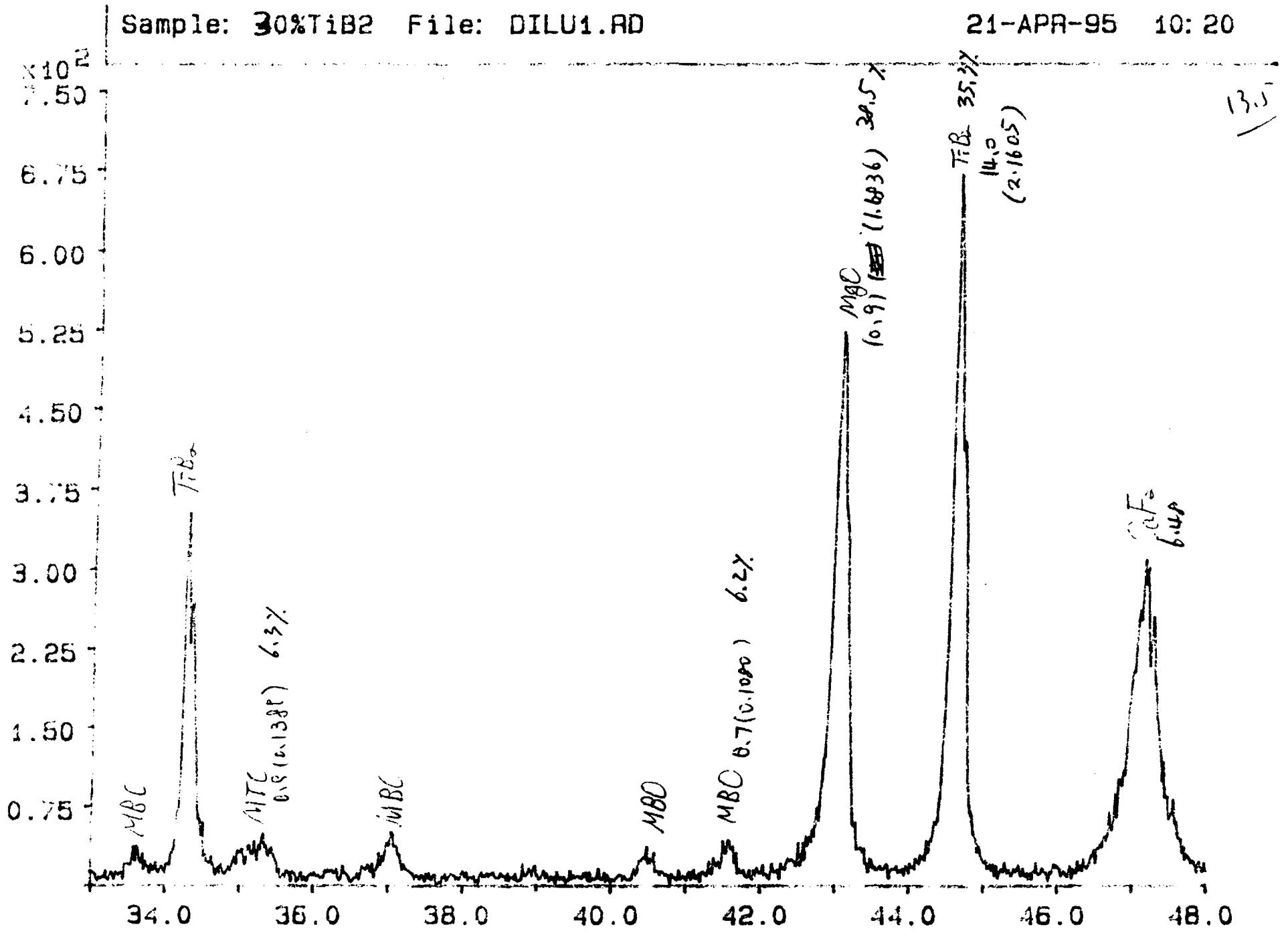

File: NISHIY.RD
22-APR-95 08: 22
x10 2
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
2.4%
?
19.8%
15.7%
15.3%
46.7

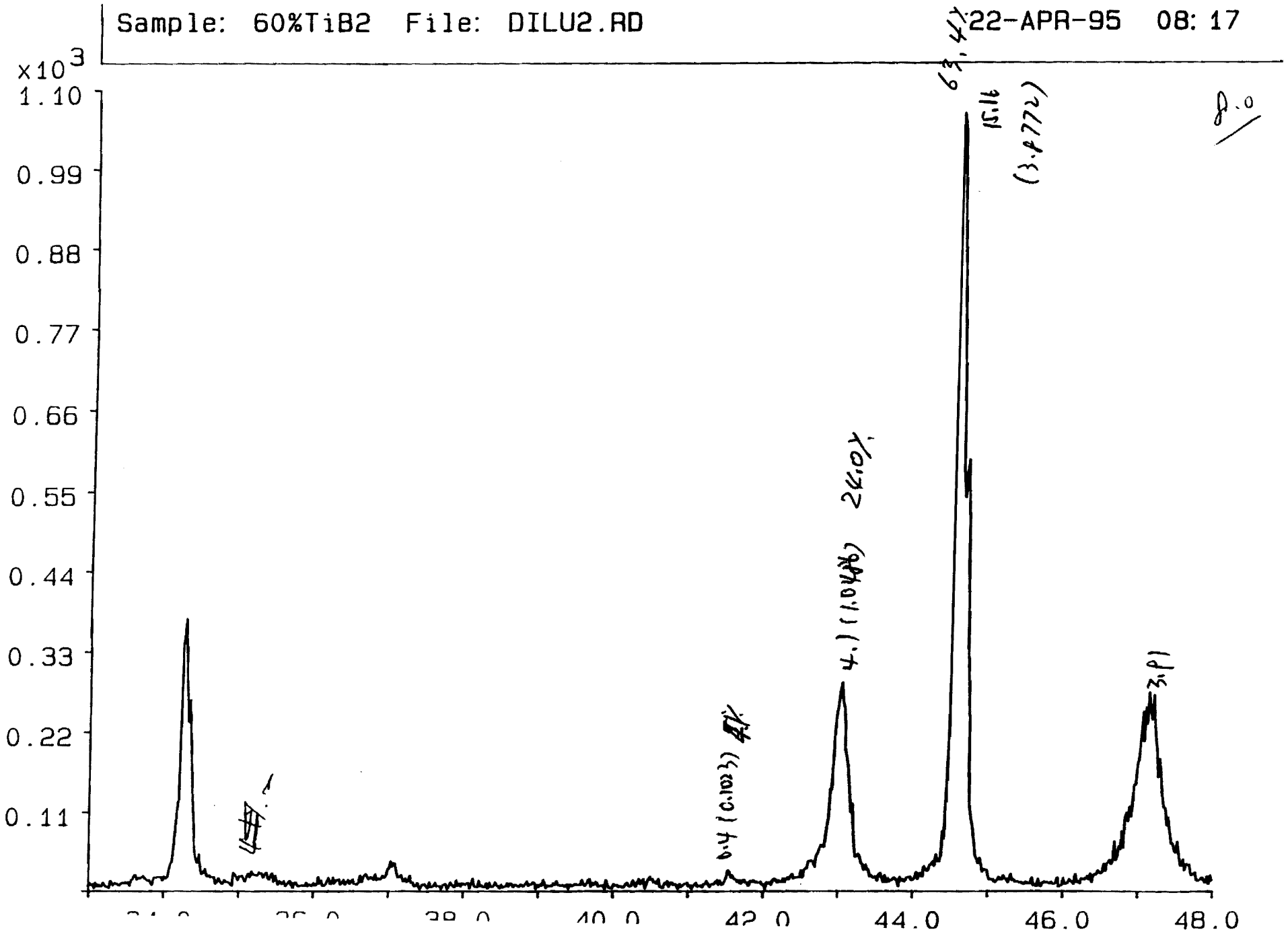
III Effect of Reaction Temperature

Sample	TiB_2	MgO	$Mg_3B_2O_6$	Mg_2TiO_4	glass
Preheated	15.6	52.0	12.3	11.7	8.5
30%TiB_2	35.3	38.5	6.2	6.3	13.5
60%TiB_2	63.4	24.0	4.03	-	8.0

Table 2: Effect of reaction temperature on the reaction products. Preheated: higher temperature than the normal reaction; 30 and 60% TiB_2: lower temperature than the normal reaction.


Sample: Preheated3M1B1T File: PREHEA.RD 19-APR-95 09:17
x10 2
9.00
8.10
7.20
6.30
5.40
4.50
3.60
2.70
1.80
0.90
1.8 (0,257) 11,7%
13 (0,213) 12,3%
16,0 (2,272) 52,0%
6.7 (0,9517) 15,6%
7,04


Sample: 30%TiB2 File: DILU1.RD
21-APR-95 10:20
X10 2
7.50
6.75
6.00
5.25
4.50
3.75
3.00
2.25
1.50
0.75
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
MBC
TiB2
MTC
MBC
MBO
MBC
MBC (0,9) (1.6836) 30.5%
TiB2 35.2%
14.0
(2.1605)
6.2%


Sample: 60%TiB2 File: DILU2.RD
22-APR-95 08:17
x10 3
1.10
0.99
0.88
0.77
0.66
0.55
0.44
0.33
0.22
0.11
63.4%
15.16
(3.4772)
8.0
0.4 (0.1023) 4%
4.1 (1.0446) 24.0%
3.91
40.0
42.0
44.0
46.0
48.0

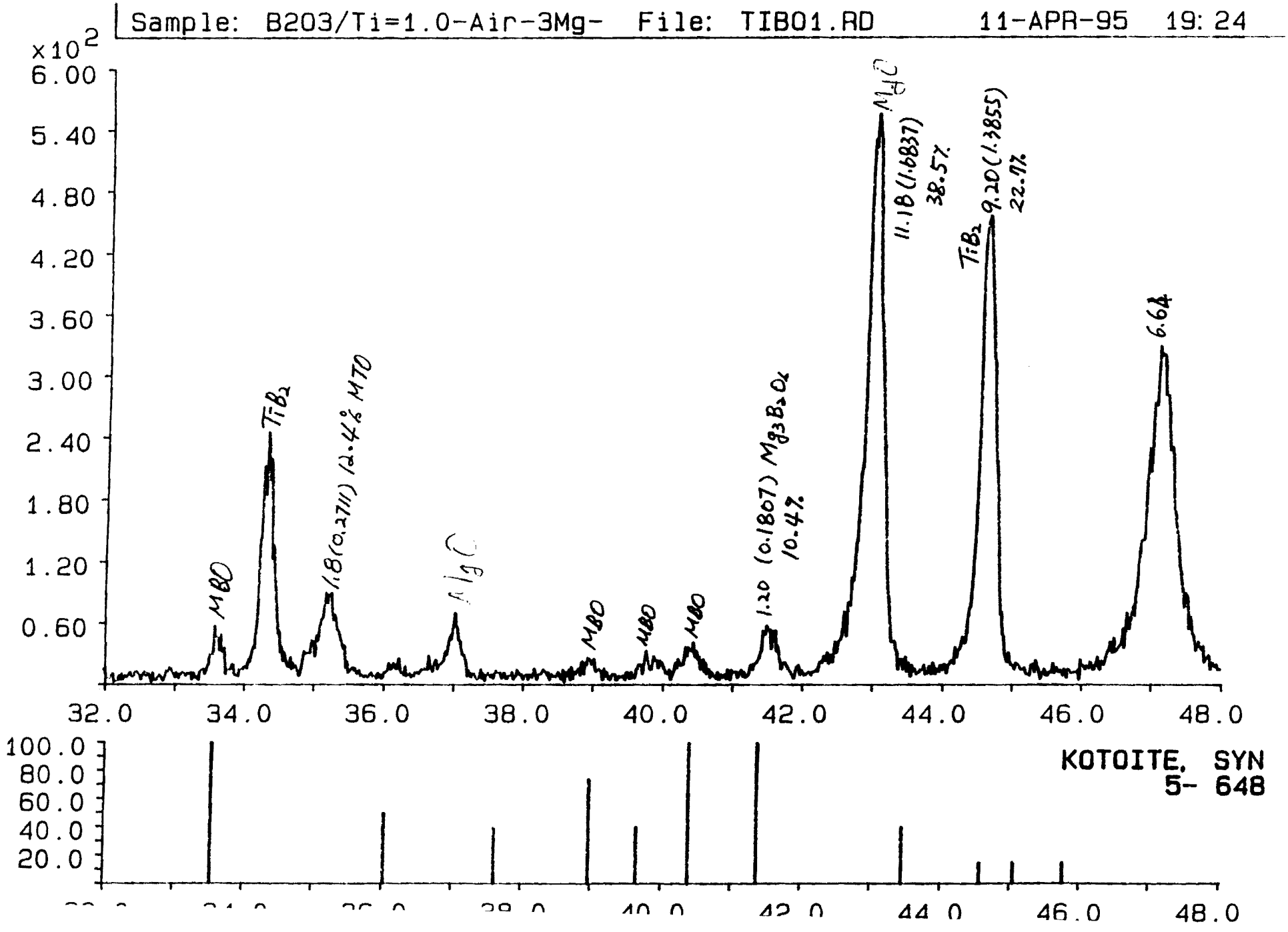
IV Different Reaction Approaches

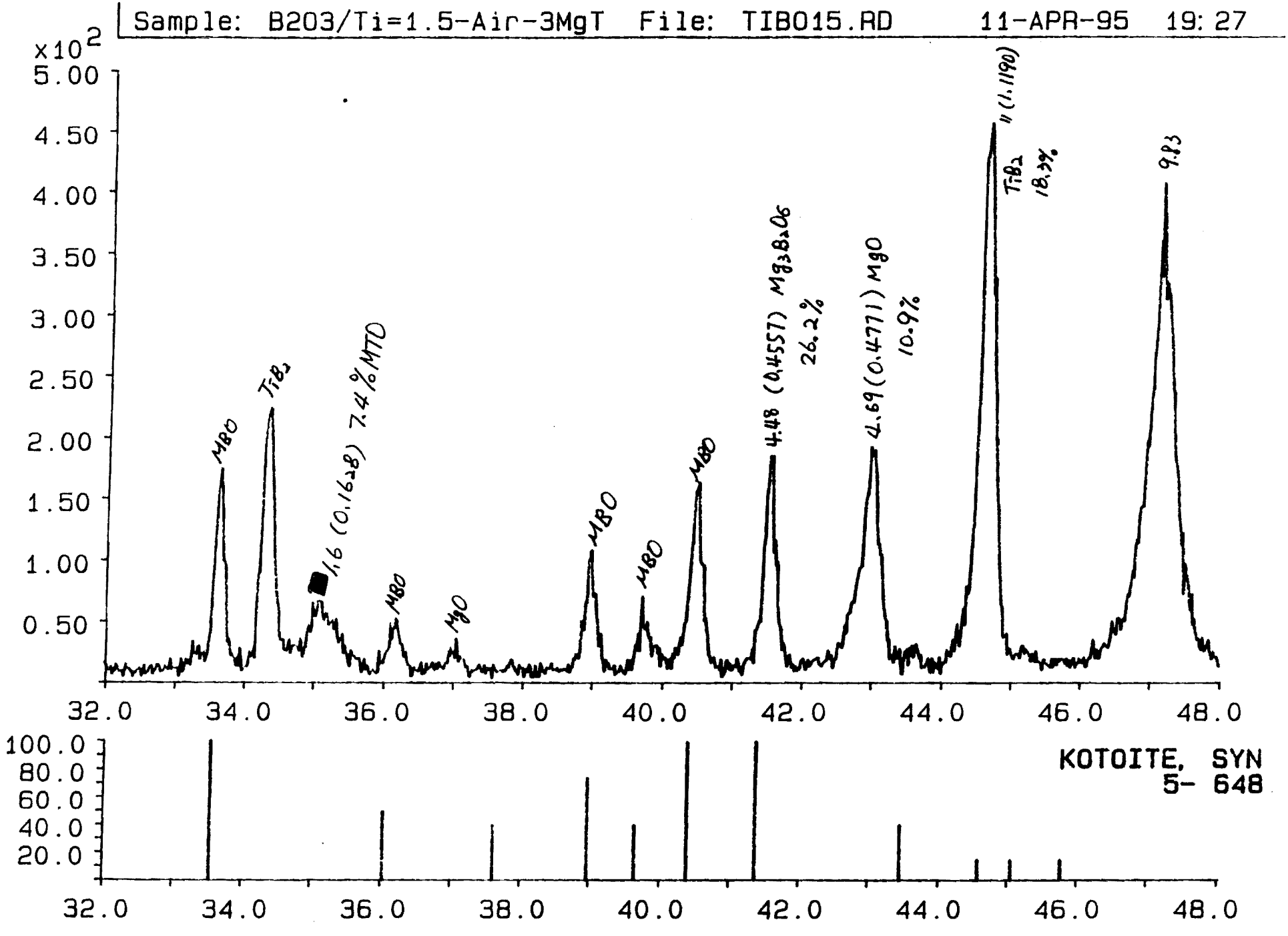
IV.1 $3Mg+Ti+B_2O_3 \rightarrow TiB_2+3MgO$

Reaction was performed in air. It was self sustaining.

Sample	TiB_2	MgO	$Mg_3B_2O_6$	Mg_2TiO_4	glass
B_2O_3/Ti=1.0	22.7	38.5	10.4	12.4	
B_2O_3/Ti=1.5	18.3	10.9	26.2	7.4	

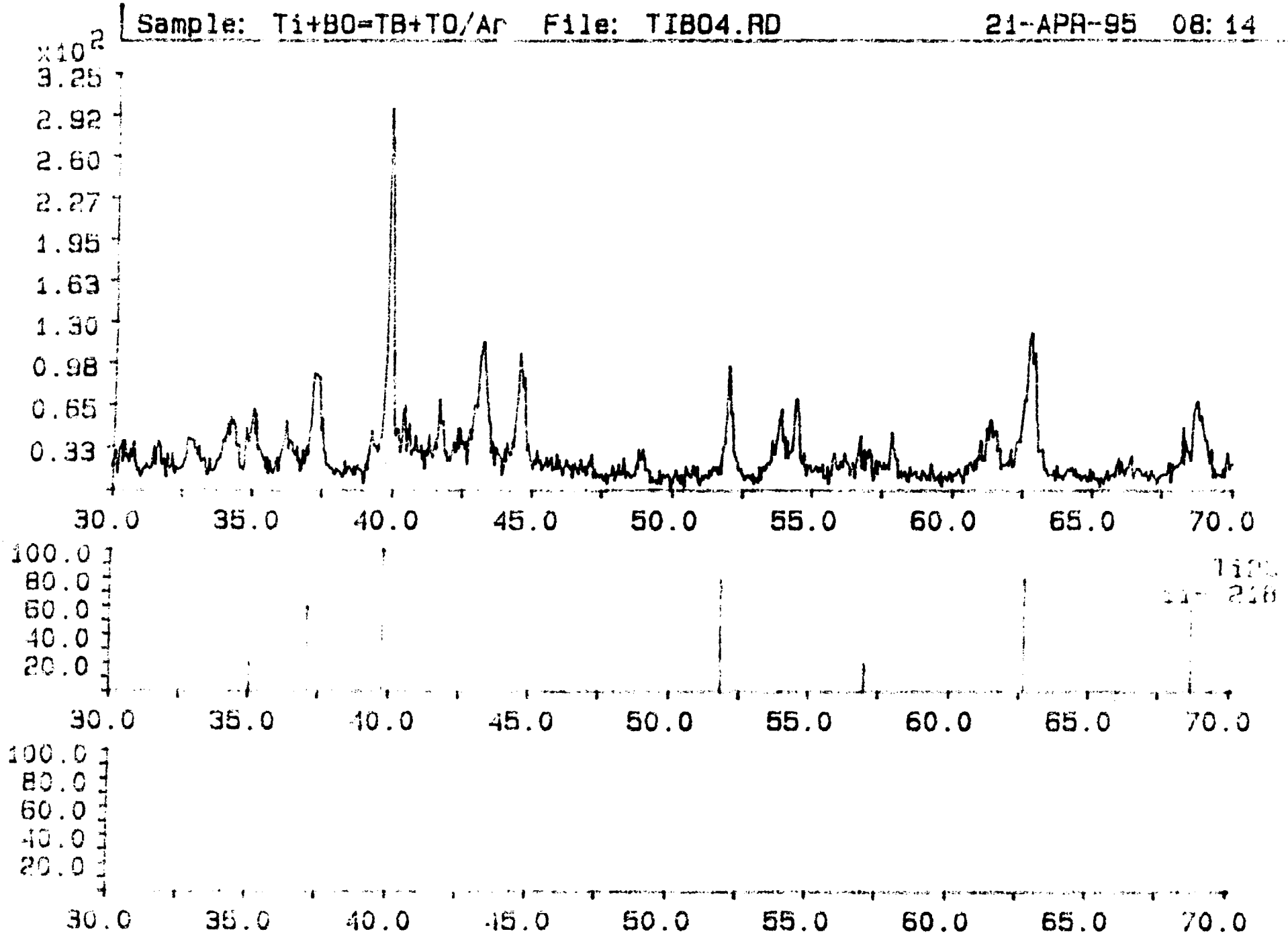
Table 3: Effect of batch composition on the reaction products. Numbers represent their weight percentages.


Sample: B203/Ti=1.0-Air-3Mg- File: TIB01.RD 11-APR-95 19:24
x10 2
6.00
5.40
4.80
4.20
3.60
3.00
2.40
1.80
1.20
0.60
MBO
TiB2
1.8(0.2711) 12.4% MTO
MgO
MBO
MBO
MBO
1.20 (0.1807) Mg3B2O4
10.4%
MgO
11.18 (1.6837)
38.5%
TiB2
9.20 (1.3855)
22.1%
6.64
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
100.0
80.0
60.0
40.0
20.0
KOTOITE, SYN
5- 648


Sample: B203/Ti=1.5-Air-3MgT File: TIB015.RD 11-APR-95 19:27
x10 2
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
MBO
TiB2
1,6 (0,1638) 7.4% MTO
MBO
MgO
MBO
MBO
MBO
4.48 (0,4557) MgB4O7
26.2%
4.69 (0.4771) MgO
10.9%
W (1.1190)
TiB2
18,3%
9.83
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0
100.0
80.0
60.0
40.0
20.0
KOTOITE, SYN
5- 648

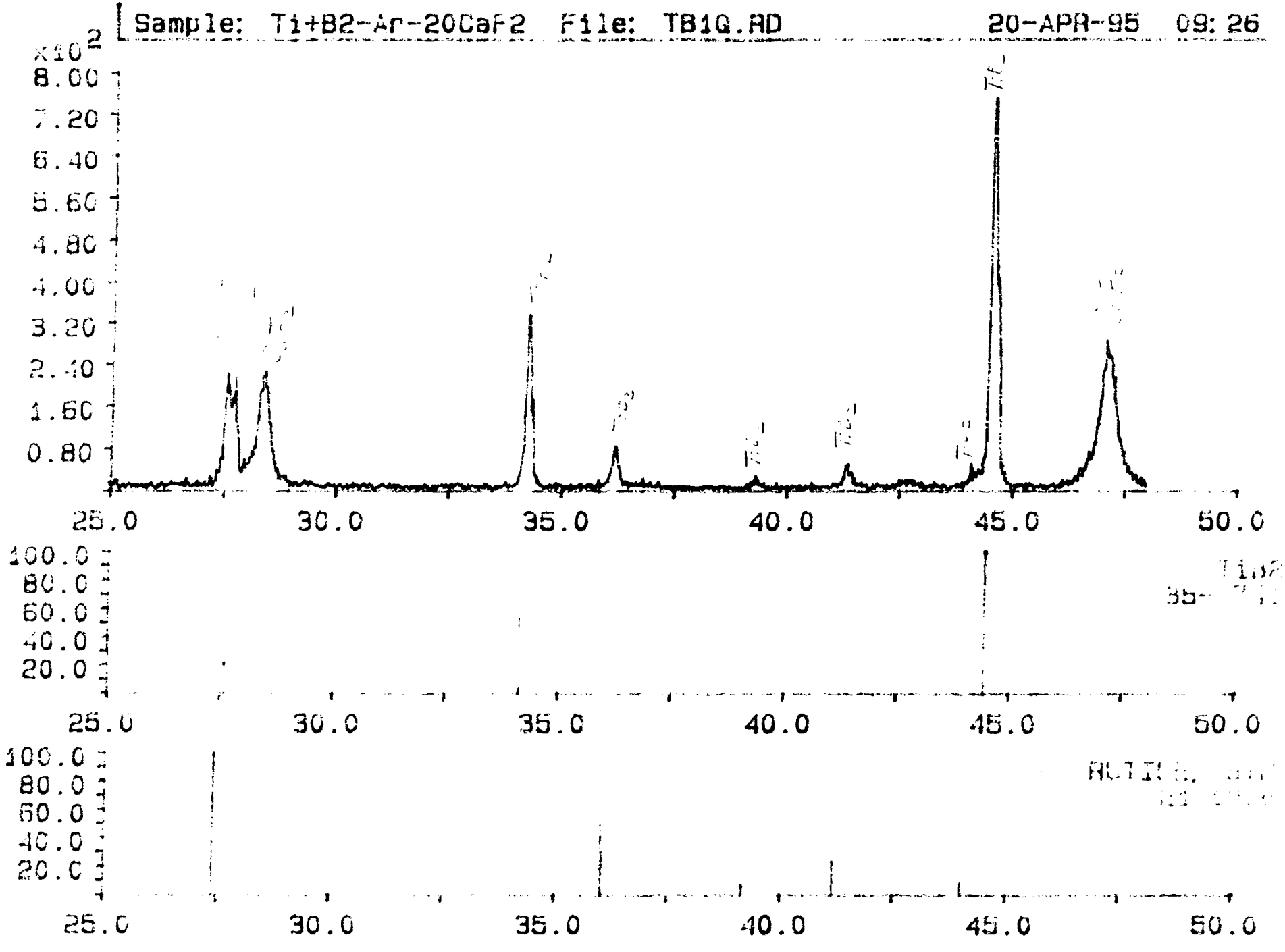
IV.2 $5Ti+B_2O_3 \rightarrow 2TiB_2 + 3TiO_2$

Reaction was not self sustaining in vacuum. Reaction was achieved in a heated vacuum furnace.

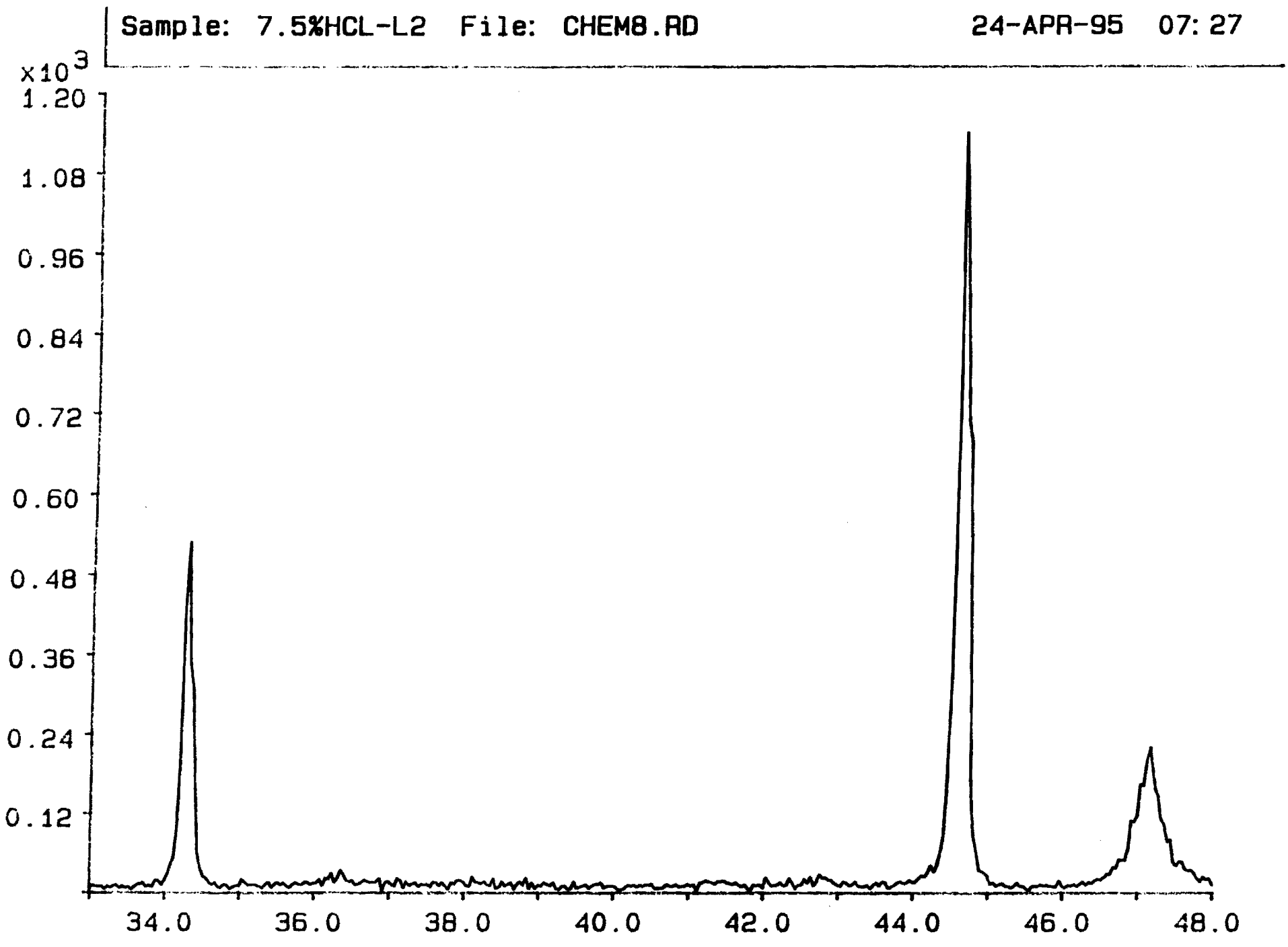

Sample: Ti+BO=TB+TO/Ar File: TIBO4.RD 21-APR-95 08:14
x10 2
3.25
2.92
2.60
2.27
1.95
1.63
1.30
0.98
0.65
0.33
30.0
35.0
40.0
45.0
50.0
55.0
60.0
65.0
70.0
100.0
80.0
60.0
40.0
20.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
65.0
70.0
100.0
80.0
60.0
40.0
20.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
65.0
70.0

IV.3 $Ti+B_2 \rightarrow TiB_2$

Reaction was not self sustaining in vacuum. Reaction was achieved in a heated vacuum furnace.


Sample: Ti+B2-Ar-20CaF2 File: TB1Q.RD 20-APR-95 09:26
x10 2
8.00
7.20
6.40
5.60
4.80
4.00
3.20
2.40
1.60
0.80
25.0
30.0
35.0
40.0
45.0
50.0
100.0
80.0
60.0
40.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
100.0
80.0
60.0
40.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0

V Chemical Leaching


Sample: 7.5%HCL-L2 File: CHEM8.RD 24-APR-95 07:27
x10 3
1.20
1.08
0.96
0.84
0.72
0.60
0.48
0.36
0.24
0.12
34.0
36.0
38.0
40.0
42.0
44.0
46.0
48.0

PROCESS PARAMETERS

rev. 2/07/95

STORAGE CONDITIONS

1. Humidity
2. Component proximity to each other

SYNTHESIS

1. Raw material blending homogeneity
2. Particle size
3. Packing density
4. Temperature of reactants at reaction initiation
5. Humidity
6. Reaction environment (Oxygen/Nitrogen/Argon)
7. TiO_2 crystallinity...anatase
8. Magnesium purity/flake
9. Aluminum purity/atomized
10. B_2O_3 purity (anhydride)
11. Reaction container cover
12. Pressure release: PV = nRT P=Pressure, V=Volume, R=constant, T=Temperature

$$\frac{P_1V_1}{P_2V_2} = \frac{n_1RT_1}{n_2RT_2}$$

13. Operations ventilation/smoke particle scrubber
14. Batch size of reaction/container size
15. Container composition: Fe, SiO_2

MILLING

1. Composite
   a. Alumina surfaces
   b. Dry
2. "Pure"
   a. Steel surfaces
   b. Dry

LEACHING

1. pH, 2.4-2.7: < 2.0=>titanates, > 8=>borates
2. Temperature > 90°C
3. HNO_3 only followed with H_2O rinse to prevent pyrophoric by-products and cause high l/d hot pressed grains
4. H_2SO_4 final wash with H_2O rinse to inhibit grain growth
5. Initial TiB_2/MgO particle size to minimize leaching time.
6. Mass/liquid volume
7. Operations ventilation
8. Particle suspension/separation

9. Particle dwell time in acid
10. Container composition: Steel (Fe), glass (SiO_2), plastic (C)

FORMING

1. Presence of glass phase (borates) as sintering aid
2. Pre-press density
3. Graphite expansion
4. Ram Travel
5. Temperature
6. Pressure
7. Temp. incr. rate/hold time (constant temperature)
8. Reducing environment
9. Pres. incr. rate/hold time (constant pressure)

FINISHING

1. Surface finish
2. Finishing surface interactions
3. Diamond/EDM

QUALITY CONTROL

STORAGE CONDITIONS

1. Moisture
2. Flame control (Magnesium/Aluminum powders): dust, sparks

SYNTHESIS

1. Mixing uniformity
2. Mixing ratio
3. Batch weights

MILLING

1. Particle size
2. Mill contaminants

LEACHING

Solution
1. Temperature
2. Mass solids
3. Volume liquids
4. Volatiles
5. pH
6. $MgNO_3$ by-product
7. Supernatant saturation

DRYING

1. @100 °C
2. Air circulation
3. Vented

Product

1. Composition
2. Particle size
3. Dry weight

FORMING

1. Temperature
2. Pressure
3. Ram travel
4. Reducing environment
5. Operator air quality
6. Time

Product

1. Weight
2. Density/porosity
3. Grain size/morphology
4. Phase distribution (T in A)
5. Mechanical properties
6. Electrical properties
7. Chemical properties
8. Thermal properties

FINISHING

1. Surface finish
2. Finishing surface interactions
3. Diamond/EDM

STEP BY STEP PROCEDURE FOR ACID-WASHING AS-REACTED TITANIUM DIBORIDE POWDER USING NITRIC ACID

Before washing:

* Wear goggles or glasses to protect eyes from acid, etc.
* Wear lab-coat to protect clothing and skin from acid.
* Wear gloves to keep acid off skin, especially when pouring the acid.
* Make sure stirrers and hot plates are plugged in and working.
* Make sure pH meters are reading accurately---follow calibration procedures in manual. (I normally calibrate the meters once a week.)

FIRST WASH:

1. Weigh out 430g of as-reacted powder.
2. Fill large beaker with about 2700-3000 ml of **hot tap water.**
3. Set beaker on hot plate and turn hot plate on to about 75% full power.
4. Place the stirrer and the pH meter in the water, turn stirrer on and pour in the 430g of powder.
5. Add 500ml of nitric acid to the separatory funnel and position it over the beaker.
6. Check the water temperature and adjust the pH meter accordingly.
7. Start adding the acid in a thin stream.
8. Increase the rate of acid addition slightly, keeping the pH of the solution above 2.0. (I tend to keep the pH about 2.5 to 4.0 for the first 500ml of acid.)
9. Refill the separatory funnel with 500ml of acid and continue washing. (Be sure to close the stopcock on the funnel before refilling.) Turn the hot plate on to full power.
10. Keep the pH of the solution between 2.0 and 2.2 for the remainder of the wash.
11. The first wash lasts for 2 hours.

NOTES:

The first 500ml of acid takes about 8 minutes to be used up. Near the end of the 500ml the water will be about 100 C and the pH should be in the 2's. Because of this, the solution will start foaming with some yellow smoke possibly occuring. You will need to slow down the acid rate to prevent the foam from spilling out the top. The foaming tends to end after about 600ml of acid has been added. The pH will stabilize here (if not sooner) and the temperature will drop (thats why you turn hot plate to full

power). Keep the pH between 2.0 and 2.2 for the rest of the wash. The temperature during the rest of the wash should stay consant at about 92 to 95 C. The yellow smoke seems to occur when the temperature is above 100 C.

12. Turn off acid, stirrers, hot plate and remove pH meter.
13. Make sure the filter apparatus is set up, and then filter the wash. Use the coarse filter paper for the first wash.
14. Scrape the collected powder off the paper and put into large beaker again.
15. Measure the amount of acid remaining in the funnel and record in the notebook the total amount of acid used.

SECOND WASH:

1. Fill beaker (from step 14 above) with about 2700 ml of hot tap water.
2. Place stirrer and pH meter in the water and adjust the pH meter to the temperature of the water. Turn stirrer on.
3. Fill separatory funnel with 100ml of acid, place over thr beaker and start adding the acid, keeping the pH between 2.0 and 2.2.
4. Periodically check the temperature and adjust the pH meter accordingly.
5. Wash takes 1 hour.
6. After wash finishes, measure the amount of acid remaining.
7. Set up filter apparatus as before, but use medium porosity filter paper this time. Filter the wash as before and scrape the powder off the paper into a labelled drying dish and let dry in the oven.

NOTES:

Ideally, the total amount of acid used in both first and second wash is 1000ml. 1000ml of acid should bring the weight of the dried powder to about 100g. If the final weight of the dried powder is 105g or less it is usually ready to be sulfer washed. However, if the powder weighs more than 105 grams, it will need to be THIRD WASHED.

THIRD WASH:

The same as a second wash.

SULFER WASH:

1. Prepare a 10% (by volume) solution of sulfuric acid and water (remember to always add acid to water, not vice versa).
2. Let cool for a while.
3. Add 2500ml of cold tap water to a large beaker.
4. Place stirrer and pH meter in the water and adjust pH meter to the correct water temperature.
5. Fill small buret with the acid solution.
6. Add powder to the water.
7. Hold buret above the beaker and add the acid full open till the pH of the wash drops to about 2.7 to 2.9.
8. Record the amount of acid taken and the lowest pH in the notebook.
9. Filter this wash as before using the medium porosity filter paper and put powder in oven to dry.

Conclusions

* Safety Issues: Potential violent results (i.e. fire/explosions) in the manufacturing process (particularly in leaching) based on significant deviations from the GIT procedure and Joel's observations of a small scale demonstration of the leaching conditions expected in the AEM plant.

* Process Parameters: The quality of the products are directly dependent on the listed process parameters. Also, substantial deviation from the GIT process can cause hazardous results in the synthesis and processing.

* Technology Transfer: At the present the composite powder and dense shapes are viable products and can be "sold." The pure TiB_2 powder is <u>not</u> a viable product due to extreme inconsistencies in the quality of powder produced in the scale-up of the leaching process. Also, the hot pressing parameters have not been well defined.

* Significant research and development needs to be continued on both the pure TiB_2 and composite TiB_2/Al_2O_3 technologies.

* Numerous prototypes for high performance applications continue to be identified.